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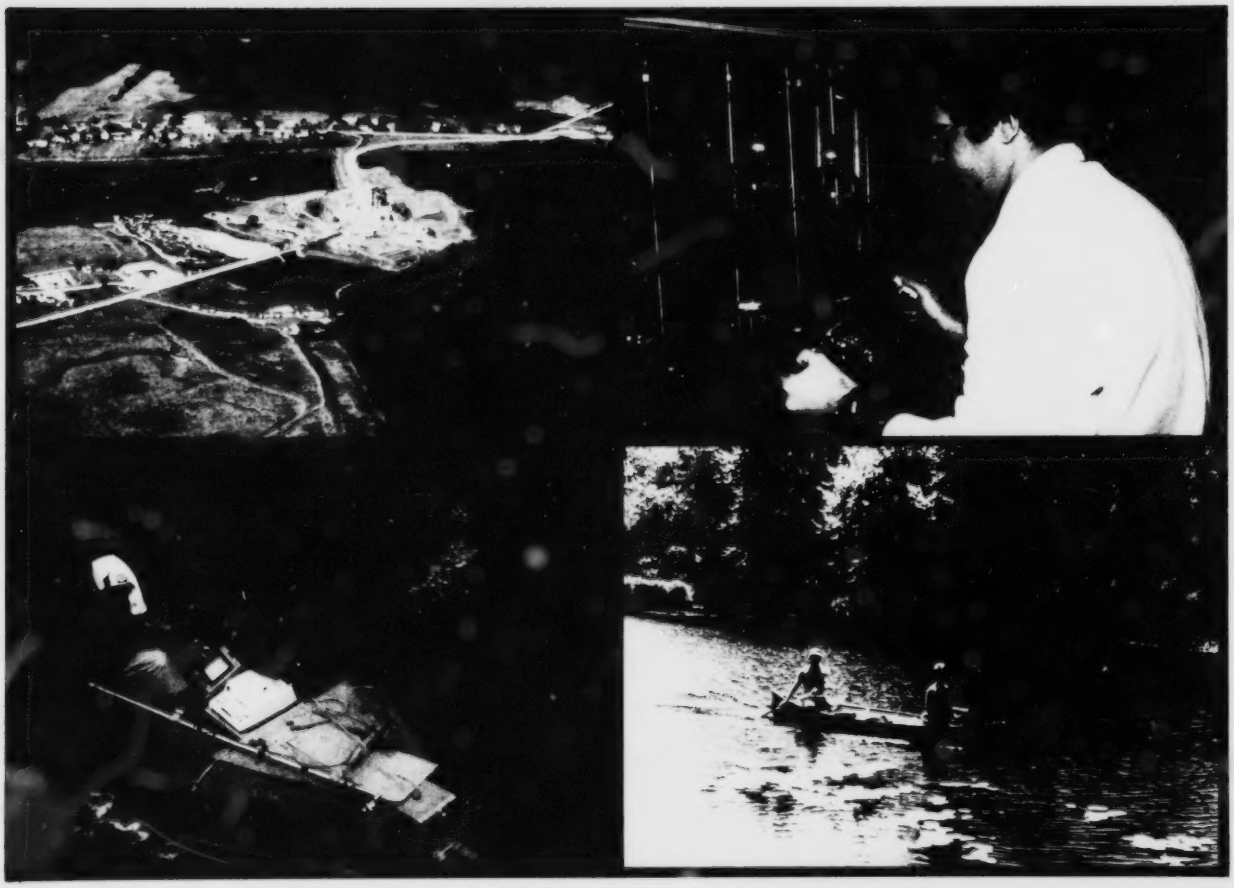
MAJOR ION DYNAMICS OF SURFACE WATERS OF VARYING HYDROLOGIC ORDER

IWD-AR-WQB-89-152



Canada

INLAND WATERS DIRECTORATE
ATLANTIC REGION
WATER QUALITY BRANCH
MONCTON, NEW BRUNSWICK

MAJOR ION DYNAMICS

OF SURFACE WATERS OF VARYING

HYDROLOGIC ORDER

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Inland Waters Directorate
Environment Canada

by

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Water Quality Branch
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ABSTRACT

The seasonal patterns of major ion chemistry for eight streams and two lakes situated in the vincinity of Kejimkujik National Park are considered. Sulphate concentrations exhibit the same seasonal pattern in all the systems investigated with minima occurring during the summer and maxima occurring during the late winter, early spring. Comparison of atmospheric deposition with river export indicates that sulphate in these systems is predominantly from atmospheric supply as annual wet sulphate deposition can account for approximately 80% of the annual river sulphate export. However, monthly sulphate budgets indicate that there is strong seasonal cycling in these systems with sulphate being retained from May to November and lost from December to April.

The DOC seasonal patterns in these systems are highly variable, with higher order systems exhibiting up to three month response lags. The low order streams have DOC maxima during the late summer and fall and minima during the spring. The much higher order rivers have DOC maxima during the winter and minima during late spring and early summer. Other terrestrially derived variables (calcium, magnesium and silica) exhibit similar seasonal patterns.

The patterns of DOC and sulphate observed indicate that both mineral and organic acids are important in the acidification of these systems. In the low order streams mineral acids dominate

during the spring while organic acids dominate during the summer. In the higher order systems there is no clear cut seasonal dominance of either organic or mineral acids. However, major changes in pH in these systems tend to be associated with changes in sulphate concentrations rather than in DOC concentrations.

RÉSUMÉ

Les variations saisonnières de la chimie des ions principaux dans huit cours d'eau et deux lacs à proximité du parc national Kejimkujik sont analysées. Dans chaque système étudié, les concentrations de sulfate sont maximales durant la saison estivale, tandis qu'elles sont minimales vers la fin de l'hiver et au début du printemps. Une comparaison entre les dépôts atmosphériques de sulfate et les quantités exportées par les cours d'eau démontre que les sulfates sont majoritairement de source atmosphérique. En effet, les précipitations humides annuelles contribuent pour environ 80% de la quantité de sulfate exportée annuellement par les rivières. Cependant, les budgets mensuels de sulfate indiquent la présence de cycles saisonniers prononcés dans ces systèmes, de sorte qu'il y a une rétention de sulfate entre les mois de mai et de novembre, et une perte, de décembre jusqu'en avril.

Les variations saisonnières du carbone organique dissous (COD) dans ces systèmes sont fortement variables. Les systèmes d'ordre supérieur exhibient jusqu'à trois mois de retard dans leur réponse. Les cours d'eau d'ordre inférieur atteignent leurs maxima en COD durant la fin de l'été et l'automne, et leurs minima pendant le printemps. Les rivières d'ordre beaucoup supérieur ont des maxima en COD pendant l'hiver et des minima à la fin du printemps et au

début de l'été. D'autres paramètres d'origine terrestre comme le calcium, le magnésium, et la silice ont démontré des variations similaires.

Les changements temporels de COD et de sulfate indiquent que les acides minéraux et organiques jouent des rôles importants dans le processus d'acidification de ces systèmes. Dans les cours d'eau d'ordre inférieur, les acides minéraux dominent pendant le printemps, alors que les acides organiques prédominent durant l'été. Dans les systèmes d'ordre supérieur, il n'y a pas de domination saisonnière bien définie entre les deux types d'acide. Cependant, les changements importants de pH observés dans ces systèmes ont tendance à être associés avec des changements dans les concentrations en sulfate plutôt que celles en COD.

INTRODUCTION

Several authors (Clair et al., 1981; Hirvonen, 1984; Howell and Brooksbank, 1986) have indicated that southwestern Nova Scotia is extremely sensitive to acidification and many studies (Kerekes et al., 1982; Howell, 1986) have shown that lakes and rivers with low pH and total alkalinity values are not uncommon in Nova Scotia. Evaluation of changes in water chemistry over time has also indicated that pH levels in lakes (Watt et al., 1979; Wiltshire and Machell, 1981) and rivers (Thompson, 1986; Howell and Brooksbank, 1986) in Atlantic Canada are presently lower than they were during the 1950's. Thus even though the present atmospheric deposition of sulphate is at or below the target loading value of 20 kg SO_4/ha.yr (MOI, 1983), LRTAP has been implicated in recent changes in surface water chemistry and has also been linked to reduced, angling yields from several southwestern Nova Scotia Atlantic salmon rivers (Watt, et al., 1983). One difficulty in ascertaining the aquatic response to anthropogenically derived mineral acid deposition is that surface waters in southwestern Nova Scotia often have appreciable sources of naturally produced acids. These waters are characteristically highly coloured by organic compounds and thus natural organic acids play a major role in the acidification process. In isolated locations, the oxidation of mineralized slates can also result in acidification by naturally produced strong mineral acids. However, this is not expected to be a widespread problem and Gridley (1986) indicates that there are low

to moderate acid mine drainage risk zones in parts of southwestern Nova Scotia.

Kejimkujik National Park is situated in southwestern Nova Scotia and encompasses an area of approximately 377 km^2. Over the last decade, numerous lakes and rivers in this area have been sampled with the intention of elucidating the chemical response of systems which are sensitive to LRTAP. As a result of these various sampling programs, there are high quality data sets available which can be used to address specific LRTAP related questions. To date, there have been several attempts to analyse these data but most of these efforts have focussed on a small portion of the available data sets or looked at specific issues related to LRTAP (Freedman et al., 1986; Kerekes et al., 1982; Kerekes et al., 1986). This report examines the seasonal dynamics of terrestrially and atmospherically derived water quality parameters at eleven sites with the intent of understanding some of the underlying mechanisms of the acidification process. These sites are all situated in the vicinity of Kejimujik National Park, have data sets spanning several years and represent a cross-section of various stream orders and water quality characteristics. As surface waters in southwestern Nova Scotia are characteristically highly coloured much of the discussion will focus on the importance of terrestrial processes and the relative importance of natural organic acidity and anthropogenic mineral acidity in the overall acidification

process. In addition, the variety of data sets included in the analysis will also enable a consideration of the effects of stream order on the seasonal patterns and response to acidification.

STUDY AREA

This report considers the water chemistry seasonal dynamics of ten surface waters and one well located within or near to Kejimkujik National Park in southwestern Nova Scotia (Figure). The surface water stations include three first order streams (Moose Pit Brook, Rodgers Brook, Atkins Brook), three streams draining one or more headwater lakes (West River, Mount Tom Brook, Whiteburn Brook), two higher order rivers (Mersey River, Little River) and two headwater lakes (Pebbleloggitch Lake, Beaverskin Lake).

Moose Pit Brook - a small highly organic low order stream which drains an area of approximately 16.7 km^2. This stream has a continuously recording gauge and has been sampled weekly since March 1983. In recent years, the upper portion of this basin has been extensively logged.

Rodgers Brook - a small organic first order stream draining an area of approximately 8.7 km^2, most of which is within the boundary of the National Park. This stream has a staff gauge and has been sampled weekly since March 1983. The drainage basin has been slightly influenced by some road-building and experimental forestry activities.

Atkins Brook - a small, highly organic first order stream which drains an area of 15 km^2 and empties into Kejimkujik Lake. This stream is accessible by boat, is not gauged and is entirely within the National Park Sampling began in 1979 at a monthly frequency until 1983 when samples continued to be collected only during the ice-free period.

West River - a large moderately organic system (120 km^2) which drains seven headwater lakes. The river is not gauged, is accessible by boat and drains into the north-western basin of Kejimkujik Lake. Sampling began in 1979 at a monthly frequency but was reduced to ice-free season sampling in 1983. Most of the drainage basin is within the National Park and is subjected to minimal anthropogenic influence.

Mount Tom Brook - a small (11.1 km^2) organic stream which drains Mount Tom Lake and empties into the western side of Kejimkujik Lake. The drainage basin is entirely within the National Park and the sampling station is accessible by boat. Monthly sampling began in 1979 but was reduced to ice-free season sampling in 1983.

Whiteburn Brook - a small (9.5 km^2) slightly organic stream which drains two headwater lakes. This system is entirely outside of Kejimkujik National Park and has been sampled weekly since 1983. The stream is subject to moderate road, agricultural and forestry activities. Discharge rates are estimated from a staff gauge.

Mersey River (at Mill Falls) - a large moderately coloured river which has a drainage area of 295 km^2, most of which is outside the park boundaries. The river has a continuous recording gauge and has been sampled at various intervals since 1979. The Mersey River is the main inflow into Kejimkujik Lake and drains a large number of major waterbodies situated to the north-east of the Park.

Little River - a large (131 km^2) moderately organic river which enters the northern basin of Kejimkujik Lake. This river drains a series of large lakes both within and external to the park. Little River is not gauged and has been sampled monthly from 1979-1983. The collection frequency was restricted to the ice-free season in 1983.

Pebbleloggitch Lake - a small headwater lake (.34 km^2) with a drainage area of 1.6 km^2 and a theoretical flushing rate of 3. times per year. This lake is situated in the southwest corner of the park and is highly organic. Pebbleloggitch Lake is not gauged and has been sampled at various intervals since 1979.

Beaverskin Lake - a small headwater lake (.43 km^2) with a drainage basin area of 1.0 km^2 and a theoretical flushing rate of 0.8 times per year. This is a clearwater lake situated 1.5 km east north-east of Pebbleloggitch Lake. Beaverskin Lake is not gauged and has been sampled at various frequencies since 1979.

More detailed information on the location and general characteristics of these basins has been presented by Kerekes et al. (1973) and Freedman et al. (1986). The well at Pebbleloggitch Lake is a shallow ($\sim$ 5 m) dug well and is used in this report to provide some indication of groundwater processes. Precipitation chemistry used in this report was obtained from the CAPMoN station (Vet et al., 1984) situated in Kejimkujik National Park.

METHODS

The samples from these surface water stations were collected by Environment Canada personnel or contract employees and all analyses were performed at the Water Quality Branch laboratory in Moncton. Samples were collected for major ions and metals in 1-L and 500 mL polypropylene bottles respectively. All bottles were acid-washed and rinsed with sample water twice before sample collection. Samples for heavy metal determination were field preserved with 0.5 mL of concentrated nitric acid and field blanks were prepared as a quality control measure. In addition, commencing in April 1984, sequential triplicate samples were collected at approximately 10-15 percent of the sites as a further quality control procedure. The field quality control/quality assurance program has been fully documented by Arseneault and Howell (1984) and results of the sequential triplicate sampling program have been discussed by Arseneault and Howell (1985).

Table 1 presents a list of the parameters for the Kejimkujik surface water sites along with the analytical parameter codes. All analyses have been performed according to the methods given in the Analytical Methods Manual (WQB, 1979). All samples were verified for ion balance and relationship to historical ranges prior to acceptance.

The water quality data were manipulated on a VAX-750 minicomputer and all the graphics and statistics have been performed using the RS/1 software package.

DISCUSSION

Silica

The major source of silica in surface waters is through the weathering of siliceous material in the drainage basin and thus silica can be used as an indicator of groundwater influence. It must be noted that silica is not entirely conservative, as it is an essential nutrient for some phytoplankton, particularly the diatoms. However as the streams and lakes in Kejimkujik National Park are generally oligotrophic, biological uptake probably results in only slight summer reductions in silica concentrations.

Silica concentrations in water from the shallow well at Pebbleloggitch Lake (Figure 2) tend to peak during September and October and reach a minimum in March and April. This pattern is essentially the inverse of the hydrograph for the first order Moosepit Brook and suggests that the seasonal pattern reflects dilution and concentration processes during recharge and discharge periods respectively. Despite these seasonal patterns, the silica concentrations remain relatively constant ranging from 3.5 mg/L to 5.5 mg/L.

The three first order streams (Moosepit, Rodgers and Atkins) have very similar seasonal patterns of silica and agree with the pattern observed in the waters collected from Pebbleloggitch Well (Figure 3). Using the Moosepit Brook hydrograph (Figure 4), it is

readily apparent that the silica dynamics are inversely related to the hydrograph. This is particularly obvious during January of 1985, where an uncharacteristically low discharge rate following a December high flow period resulted in secondary silica peaks in both Moosepit and Rodgers Brook. The linear regression correlation co-efficient of -0.58 between daily mean discharge and silica concentration for Moosepit Brook also indicates an inverse relationship but due to lag effects and the highly variable hydrograph, the relationship is not particularly strong.

The three first order streams all exhibited similar concentration ranges and except for higher maxima they also paralleled the silica range observed in groundwater. The elevated silica peaks in these surface waters have several possible explanations. It is possible that siliceous material in the soil overburden of these basins is more abundant than in the recharge zone of the groundwater station. An alternate explanation is that evapo-transpiration during low summer and autumn flow periods serves to further concentrate the surface water silica concentrations relative to groundwater. In addition to these two possible explanations, there is the possibility that the peak values are affected by analytical interferences. The silica method presently employed is a colourimetric technique using an aluminum molybdate colour indicator. This method is known to be susceptible to interference in waters high in tannins, iron, colour, turbidity, sulphide and phosphate. As the three streams are highly coloured and the dissolved organic carbon peaks coincide with the silica

peaks, it is very possible that some of the observed silica during the fall is due to organic interference. The similar silica minima observed for the streams and the well suggests that the groundwater and surface waters are closely linked and are under the control of the same dilution process during high flow conditions. Also as the minima are much greater than the silica values observed in precipitation, it appears that even during high flow periods, there is sufficient interaction time between precipitation and the drainage basin to allow some chemical weathering.

Figure 5 presents the seasonal patterns of silica concentrations in three streams (West River, Mount Tom Brook and Whiteburn Brook) which drain one or more headwater lakes. These streams exhibit seasonal patterns which are similar to those observed for the first order sites except that the timing of the extremes is less distinct. However the concentration ranges of these sites are quite different from the first order streams, having minima of approximately 1.0 mg/L and maxima of 9.0 mg/L. These maxima are only slightly greater than the groundwater peak values which suggests that either evapo-transpiration is less important or that there is less organic interference. Either of these explanations is possible as the lake storage potential may serve to reduce the influence of evaporation and all three sites are less coloured than the first order streams. The minimum values occur during high flow periods and are at levels intermediate to precipitation and groundwater. This suggests that under elevated discharges, these streams have much less interaction with the

groundwater than the first-order streams and thus chemical weathering is reduced.

Figures 6 and 7 present the silica patterns for two high order rivers (Little and Mersey) and two headwater lakes (Beaverskin and Pebbleloggitch). These systems have maximum silica concentrations during December to February, which is approximately three months after the lower order systems peak. Similarly, the minima are also delayed by approximately 3 months being observed from June to September. Comparison of silica dynamics with the Mersey River hydrograph indicates a very different relationship between discharge and silica concentration than was observed for the lower order systems. During high flow periods in late winter and early spring, dilution by surface runoff begins rapid decreases in silica concentrations which extend well into summer baseflow conditions. The fact that the surface water silica minimum values are observed under low flow conditions indicates that the storage potential of these high order systems and lakes provides a continued supply of dilute waters during periods when groundwater influences would be expected to dominate. In addition, it is possible that uptake of silica by diatomaceous phytoplankton in these higher residence time systems may also be implicated in the low summer silica concentrations. As base flow conditions continue into the fall, silica concentrations begin to increase slowly in response to concentration of surface waters by evaporation or possibly increases in groundwater influence.

In conjunction with the ascending leg of the hydrograph (Figure 8) during late fall, silica concentrations increase dramatically and peak during early winter. This is interesting as it demonstrates that these higher order systems can have inconsistent responses to elevated flow conditions. During high flow in the late winter, frozen soil limits the interaction between runoff and the terrestrial basin and thus surface water concentrations tend to reflect values observed in precipitation. However, following baseflow conditions, the increased autumn flow appears to recharge the system which increases soil-water interactions and flushes silica into the surface waters.

The silica ranges observed in these high order systems are much less dramatic than in the first order streams, and reflect their greater storage capacities and water residence times. This is particularly evident for Beaverskin Lake which has a water residence time of one year and silica concentrations which are always less than the values observed in groundwater. The other systems have maximum values which are very similar to the groundwater peaks and minima that are similar to concentrations observed in precipitation.

Dissolved Organic Carbon

Surface waters in southwestern Nova Scotia are characteristically highly coloured and thus the input of allochthonous organic acids may play an important role in the overall acidification process.

The first-order streams and those draining small headwater lakes (Figures 9 and 10) exhibit very similar seasonal patterns with the dissolved organic carbon maxima occurring during late summer and early fall and the minimum values being observed from February to April. When compared to the hydrograph, it is apparent that DOC concentrations and discharge at Moosepit Brook are inversely related, having a correlation co-efficient of -0.46. This relationship indicates that discharge can only explain a small percentage of the DOC variability and that processes other than dilution are involved. As allochthonous organic carbon is largely derived from exudates and degradation products of terrestrial vegetation, the supply of organic carbon should be greater during the growing season. This coupled with low flow conditions during the summer and early fall explain the elevated organic carbon concentrations observed during this period. However, as low flow conditions continue into the fall, the DOC concentrations begin to decrease, which is a departure from the expected inverse relationship with discharge. In fact, the peak DOC concentrations appear to be associated with small discharge pulses during the summer and fall which suggests that a certain minimum discharge

value is required to flush the organic compounds from the drainage basin into the receiving waters. The continuation of the low flow conditions in the autumn corresponds to the peak in silica concentration and thus the observed decreases in DOC concentrations may reflect increased involvement of groundwater which is low in dissolved organic carbon. This decline in DOC continues throughout the winter as higher discharge increases the dilution of terrestrially derived material and the freezing of the soil overburden decreases the interaction between runoff and soils. Thus the dissolved organic carbon dynamics in lower order systems are ultimately driven by the hydrologic regime but other factors which control the availability and transport of organic carbon compounds modify the seasonal patterns.

The dissolved organic carbon seasonal patterns for the higher order streams (Figure 11) and the headwater lakes (Figure 12) exhibit variable response lags which is ascribed to system water residence time. The Mersey River shows the greatest response lag with peak DOC concentrations being observed during December and January, almost three months after the first order stream maxima were observed. The increase in DOC concentration takes place over approximately a six month period and begins during a period of moderate flow following spring runoff. As flow rate decreases, the DOC concentrations continue to increase presumably in response to reduced dilution and increased organic carbon supply during the growing season. As was noted for the first order streams, the Mersey River experiences numerous summer peaks in DOC

concentrations which appear to be associated with discharge pulses. However, unlike the lower order systems, as low flow conditions continue during the fall, the Mersey River DOC concentrations continue to increase. This suggests that even under extremely low flow conditions, the Mersey River Basin has sufficient water residence time to minimize the influence of groundwater. As flows increase during the late fall and early winter, the DOC concentrations peak in conjunction with recharge of the terrestrial watershed and flushing of the accumulated allochthonous organic matter.

The Mersey River exhibits a rather rapid response to the increased flow during the late winter and early spring, with the DOC concentrations reaching a minimum in less than three months. As both silica and DOC are predominately terrestrially derived and the decreases in concentrations are the result of dilution during spring runoff, it would be expected that the silica and DOC minima would occur at the same time. However, the DOC minimum values are observed during March and April and precede the silica minima by approximately three months. The Mersey River has numerous chain lakes in the system and thus has sufficient water residence time to enable the development of a stable phytoplankton community. As primary production increases during the growing season, autochthonous organic carbon concentrations can also be expected to increase which may serve to counteract the effects of dilution during moderate runoff. In addition, increases in diatomaceous phytoplankton during the summer may serve to reduce reactive silica

concentrations beyond the effects of simple dilution. Thus, it is entirely possible that the combination of dilution and primary production processes in higher order systems may explain the differences in the timing of the DOC and silica minima. Grafton Brook which drains the non-headwater Grafton Lake has a seasonal pattern that is similar to that observed for the Mersey River, while the Little River peaks a little bit earlier. The two headwater lakes also exhibit somewhat different seasonal patterns. Beaverskin Lake exhibits a pronounced DOC peak during the summer, similar to that observed in the lower order streams. However, as this lake is not coloured, much of the DOC is expected to be of autochthonous origin and thus increased summer primary production can have a significant influence on the seasonal pattern. Pebbleloggitch Lake has a seasonal pattern which is somewhat intermediate to the first order and the higher order streams. Although there are pronounced summertime DOC peaks there is also evidence of high values during the late fall and early winter.

Though the concentration ranges of silica are useful as indicators of groundwater influence, the DOC concentration ranges are extremely basin specific as they are dependent on the relative proportion of bog drainage. However, in general, the first order streams exhibited the most organic influence with Atkins Brook, Moosepit Brook and Mount Tom Brook having the highest DOC concentrations. The lowest DOC ranges were observed in the higher order systems such as the Mersey River and Little River and in the two headwater lakes.

Sodium and Chloride

Feth (1981) has indicated that chloride release rates from non-evaporite rocks are slow and that soils cannot generally be considered as a significant source of chloride. However, Juang and Johnson (1967) suggest that chloride may be involved in ion exchange processes in the soils particularly with the clay and humic colloids of podzolic soils. Sodium is weakly bound to soils and can move through the soil profile easily (Frink and Voigt, 1975) and thus concentrations in surface waters may be influenced by cation exchange processes and weathering of soil derived sodium (Overrein et al., 1981). Teigan et al. (1976) observed both retention and leaching of sodium in acidic lysimeter soils depending on soil type and the pH of the application water while Foster et al. (1986) estimated the annual leaching of sodium from podzolic soils in a hardwood forest to be approximately 5 kg/ha.yr. However Johnson and Cole (1975) noted minimal leaching of cations from podzolic profiles in Washington and Tamm et al. (1975) observed that increased acidification of acidic lysimeter soils in the Lisselbo basin in Sweden resulted in only slight increases in the leaching of sodium. The results of these studies indicate that leaching of sodium from soils is a basin specific process and that particularly in coastal areas this source of sodium probably comprises only a small percentage of the annual input to surface waters.

The underlying geology of the Kejimkujik National Park area is predominantly Devonian granites and Meguma series slates which are covered by thin acidic soil overburdens. Thus the geological sources of chloride and to a lesser extent sodium can be expected to be minimal. Given that the Kejimkujik basins are only 50 km from the coast, the major source of sodium and chloride is from the atmospheric deposition of marine aerosols which coupled with their apparent conservative nature has prompted their use as tracers of hydrologic and atmospheric processes.

If the sodium and chloride concentrations in surface waters are predominantly of marine origin, then there should be good agreement between atmospheric deposition and river export. From Figures 13 and 14 it is obvious that wet deposition can account for only 30% of the annual Mersey River export of sodium and chloride, which agrees with the previous findings of Kerekes et al. (1982) and Freedman and Clair (1987). This phenomenon has also been noted in other basins such as Hubbards Brook (Juang and Johnson, 1967) and Birkenes (Braekke, 1976) where the chloride output to input ratios were 1.5 and 1.6 respectively. These poor sodium chloride budgets indicate that either dry deposition, geological sources or road salt applications contribute significant loads of these ions to surface waters in southwestern Nova Scotia. Given the geological structure and the undeveloped nature of the Kejimkujik area it is probable that dry deposition is a major source of sodium and chloride. Comparison of wet and bulk precipitation chemistry (Figure 15) indicates that chloride concentrations in bulk

precipitation are often much greater, particularly during the late summer, fall and early winter. Although bulk collectors often have poor collection efficiencies (Galloway and Likens, 1975), in this case the data can be used to give an indication of some combination of wet and dry precipitation. Thus it appears that dry deposition may account for a major portion of the annual sodium and chloride load. Several authors have noted much higher sodium and chloride concentrations in bulk precipitation than in wet (Galloway and Likens, 1975; Duncan et al., 1986; Chan and Perkins, 1987), while others have noted further elevation of sodium and chloride concentrations in throughfall samples collected under the forest canopy (Dovland et al., 1976; Eriksson, 1960; Johannes et al., 1986; Freiesleben and Rasmussen, 1986). Table presents bulk and throughfall chemistry for the Kejimkujik area and indicates that impaction with the forest canopy serves to greatly elevate the sodium and chloride concentrations.

The seasonal dynamics of chloride concentrations in the Kejimkujik streams (Figures 16 to 19) were similar, regardless of stream order. All systems reached maximum chloride concentrations during January and February and minimum concentrations from April to June. In addition, all the streams had secondary peaks during October and November, although these were more pronounced in the lower order streams. The patterns in the two headwater lakes are rather obscured due to the water residence time of these systems, but Pebbleloggitch Lake does exhibit chloride peaks in January and February. The well at Pebbleloggitch Lake (Figure 20) exhibits a

distinct chloride peak during early fall but does not have the winter peak observed in the streams. The groundwater minima is quite variable, being observed from January to April.

Comparison of the chloride concentrations with the hydrograph for a first order stream (Moosepit Brook) and a high order river (Mersey River) indicate that there is generally an inverse relationship. The autumn peak in Moosepit Brook chloride concentration coincides with baseflow conditions and the period of peak concentrations in groundwater. However, as was noted for DOC, the peak values appear to depend on small pulses in discharge which suggests that the elevated concentrations are partially due to the inwash of chloride in surface runoff. The bulk precipitation data indicate that dry deposition may be prevalent during the fall and early winter and thus it is likely that small precipitation events may result in runoff with high chloride concentrations. As discharges increase during the late fall, the concentrations of chloride begin to decrease in response to increased dilution and a wash-out of the dry deposition chloride which accumulated during the summer.

With the onset of winter conditions, the drainage basin freezes, discharge rates decrease and atmospherically derived chloride is tied up in the snowpack. Roussel and Clair (1987) and Clair (1986) have shown that chloride concentrations in snow can be extremely high, particularly during the early part of the winter. As the discharge increases with the onset of the first melt, the

chloride concentrations of Moosepit Brook also peak. During the winter of 1984-1985, chloride concentrations in the snowpack reached a maximum of approximately 650 ueq/L by January 20 but by February 9 decreased to about 300 ueq/L due to addition of less concentrated snowfalls. Over the last two weeks of February, this chloride was released during a melt period which resulted in increased river discharge and elevated chloride concentrations. Similarly, during the winter of 1985-1986, snowpack chloride concentrations reached a maximum of approximately 200 ueq/L during December and early January. Commencing on January 18, 1986, a five day thaw resulted in a significant snowmelt, which corresponds to the winter peak in Moosepit Brook chloride concentrations.

Although additional snowpacks may accumulate during the winter, the chloride concentrations are without exception much lower. As a consequence of this, the final spring melt results in increased discharge rates and decreased river chloride concentrations. As the discharge increases during spring runoff, the chloride concentrations continue to decline and reach a minimum during May and June.

It is interesting to note that the Pebbleloggitch well water chemistry does not reflect the influence of snowmelt. This is presumably a consequence of a frozen soil profile which reduces soil permeability and effectively isolates the groundwater from the snowmelt runoff.

The higher order Mersey River has a very similar seasonal pattern of discharge and chloride concentration with the exception that the fall peaks are much less distinct. As was noted for silica and DOC concentrations, it appears that the rather extensive water storage potential of the Mersey River basin is sufficient to damp the effects of evapotranspiration and minimize groundwater influences. The winter chloride peaks, however, are pronounced and occur at the same time as those observed in Moosepit Brook which indicates that atmospherically controlled processes during high flow periods are sufficient to dominate the water chemistry of the Mersey River.

Chloride concentration ranges are extremely similar for many of the basins, ranging from 3.0 to 7.0 mg/L. Rodgers Brook and Whiteburn Brook exhibit higher winter maxima, 9.0 mg/L and 12.5 mg/L respectively, which may be due to runoff of road salts as both of these stations are sampled at highway bridges. The Mersey River may also have some road salt influence, but due to the size of the drainage basin there is no significant effect on the winter maximum concentrations. It should be noted that these three systems have chloride concentrations which are generally slightly greater than those observed for the other Kejimkujik basins. This suggests that Rodgers Brook, Whiteburn Brook and the Mersey River may have some terrestrial sources of chloride.

The seasonal dynamics of sodium are very similar to those observed for chloride and thus it is not necessary to discuss the

patterns and driving mechanisms in detail. However, the seasonal plots of sodium concentrations (Figures 21 to 25) do indicate that there are some subtle differences in the observed patterns. The fall peak in sodium is somewhat more pronounced than that observed for chloride and often overshadows the winter snowmelt peak. In addition, summer sodium concentrations appear to increase in advance of and at a greater rate than chloride concentrations. Figures 26 to 29 present the seasonal variations of Na/Cl ratios for selected Kejimkujik streams and indicate that except for a short period during spring runoff the values are much higher than the expected seawater ratio. Thus it appears that these systems have either additional sodium sources or have chloride sinks. Higher than expected ratios of sodium to chloride have previously been documented for Atlantic Canada lakes by Peterson (1980). It is interesting to note that the highest sodium chloride ratios in the Kejimkujik systems occur during the summer and fall when productivity of the forest ecosystem is at a maximum and dry deposition is expected to be important. The sodium chloride ratios in snow samples are generally at or below the expected seawater ratios and correspond to the period when the rivers have ratios near to the expected value. Figure 30 presents the relationship of sodium to chloride in wet precipitation collected at Kejimkujik National Park and indicates that the relative concentrations in rain are similar to the expected seawater ratio. However, the concentrations observed for the APN air network, the Beaverskin lake bulk collector and the Canadian Forestry Service throughfall samples (Figure 31), fall below the theoretical seasalt line

indicating that there is an excess of sodium in precipitation samples that include a dry deposition component. The snow samples which also represent a combination of wet and dry deposition are an obvious exception and suggest that dry deposition during the winter is either of minimal importance or has a sodium chloride ratio similar to that observed for wet deposition. Galloway and Likens (1975) observed that from December to April, the ratio of bulk to wet sodium was 4.1 while the ratio of bulk to wet chloride was 2.9. Similarly Duncan et al. (1986) observed that percent differences between bulk and wet sodium and chloride concentrations were 45% and 21% respectively. These studies indicate that bulk precipitation may during certain periods of the year be either enriched in sodium or deficient in chloride compared to the expected seasalt ratio. Whether this elevation of sodium relative to chloride in dry deposition is solely an atmospheric process or is related to impingment on the forest canopy is as yet unclear. Gosz et al. (1973) have noted that sodium does accumulate in plant tissue and Attiwill (1967) observed that sodium could be easily leached from leaf surfaces. Johannes et al. (1986) reported that increases in sodium concentrations under the forest canopy could be attributed to leaching of sodium from leaves rather than a physical wash-off process. Both Gosz et al. (1973) and Reuss (1976) noted elevated sodium concentrations in leaf and branch litter and Mayer and Ulrich (1975) recorded a sodium/chloride ratio of .88 in beach litter which is well above the expected .56 seawater ratio. These observations indicate that sodium can be accumulated and released by vegetation and it is likely that these processes can

significantly influence the seasonal dynamics of sodium concentrations and sodium chloride ratios in surface waters. Likens et al. (1970) indicated that chloride is not significantly accumulated in forest ecosystems but Peterson (1980) has noted that chloride is the main anion in cell sap. Similarly, Frink and Voigt (1975) observed that 29% (9 kg/ha) of the chloride applied to an agricultural test field ended up in the tobacco crop as compared to 7% (6 kg/ha) for sodium. Johannes et al. (1986) noted that the increase in chloride concentrations in throughfall could be attributed solely to the washoff of dry deposition impinging on the forest canopy. These studies suggest that chloride, like sodium, can also accumulate in vegetation but may not be as easily leached from plant tissue. Thus it appears that neither sodium nor chloride is entirely conservative and that biological processes may influence the surface water seasonal patterns.

The question of whether or not chloride is a conservative element is particularly important in LRTAP studies as chloride has been used extensively to correct sulphate and basic cations for marine influences. It should be noted that while most (70%) of the chloride input into the Kejimkujik basins is from dry deposition, nearly 80% of sulphate input can be accounted for by wet deposition. Thus the chloride correction is only valid if the theoretical marine SO_4/Cl ratio applies to both wet and dry deposition and the time lag between deposition and delivery to the surface waters is identical for wet and dry deposited ions. In addition if chloride is involved in processes such as uptake by

vegetation which affect the seasonal cycle then the application of a seasalt correction may be erroneous.

Calcium and Magnesium

While silica and dissolved organic carbon concentrations in surface waters of Altantic Canada are derived almost totally from within the drainage basin, and sodium and chloride concentrations are predominantly of marine origin, the calcium and magnesium concentrations reflect a combination of marine aerosol and terrestrial weathering sources. On an equivalent basis, seawater concentrations of magnesium are five times greater than calcium and therefore the seasonal dynamics of magnesium concentrations in rivers in Atlantic Canada can be expected to exhibit considerable marine influences. In addition to affecting seasonal dynamics, marine originated ions can also be involved in numerous chemical, physical and biological processes and thus are important components of the biogeochemical cycle. In an attempt to assess the innate ability of the terrestrial basin to buffer acidic components, it has been common practise to remove the marine contribution of these cations using a chloride correction. However the previous section has noted that this approach may be in error and thus the following section will concentrate on uncorrected data. It is worth noting that seasalt corrected plots were calculated for some of these basins and although the magnitudes were lowered the seasonal patterns were not significantly altered.

Calcium concentrations in water from the shallow well at Pebbleloggitch Lake (Figure 32) exhibit maxima during August to October, minima from January to April and have concentrations

ranging from 0.7 to 2.5 mg/L. The seasonal pattern is very similar to that observed for silica which suggests that the concentrations are a function of hydrology and terrestrial weathering.

The first order streams and the streams draining headwater lakes (Figures 33 and 34) exhibit similar calcium dynamics with maximum values being observed from July to October and minimum values being recorded from February to May. As the marine component of calcium is relatively small, the seasonal calcium dynamics of surface waters should exhibit patterns which are similar to other watershed derived parameters such as silica and DOC. In fact since divalent cations such as calcium complex with organic ligands (Clymo, 1963), a good relationship between DOC and calcium concentrations can be expected. This is indeed the case, with the calcium dynamics being very similar to those observed for DOC, except that calcium exhibits more pronounced winter peaks. These winter peaks correspond to periods of elevated silica levels and reduced discharges and may indicate concentration of surface waters or possibly some marine influence. The fact that the calcium maxima coincide with both DOC and silica peaks suggests that calcium concentrations in first order streams are a function of both terrestrial weathering and ion exchange processes. The calcium concentration ranges in these streams are essentially identical with the minimum (0.3-0.6 mg/L) and maximum values (1.6-2.2 mg/L) being slightly less than those observed for Pebbleloggitch well.

As was noted for the other terrestrially derived parameters, the higher order systems (Figure 35) exhibited varying degrees of response lag. As would be expected the Mersey River exhibits the most pronounced lag, having calcium peaks during December and February and minima during April and May. These patterns agree rather well with the seasonal dynamics of both DOC and silica and once again indicate that the large residence time of the higher order systems serve to obscure the seasonal major ion dynamics. The other high residence time systems such as the Little River and the headwater lakes (Figure 36) also exhibit lags in calcium peaks but these are not as pronounced as those observed for the Mersey River. The concentration ranges in the two higher order streams tend to be smaller than the first order systems with most observations falling between 0.5-1.4 mg/L. The two headwater lakes exhibit by far the least calcium variability having concentrations ranging from 0.2 to 1.0 mg/L.

Magnesium has a more significant marine component than calcium and thus the seasonal dynamics would be expected to reflect a combination of both terrestrial weathering and marine aerosol processes. The magnesium concentrations in water collected from Pebbleloggitch Lake well (Figure 37) exhibit a similar pattern to that observed for calcium, with the peak values observed during September and October and the minimum values occuring during January to April. Thus, as was apparent for sodium and chloride, freezing of the terrestrial basin appears to isolate the groundwater from wintertime inputs of marine originated magnesium.

With the exception of the Mersey River, the various systems (Figures 38 to 41) exhibit similar seasonal dynamics of magnesium having peak values during the fall and early winter and minima from February to April. These patterns are similar to those observed for calcium, except that there is a slight indication of elevated magnesium concentrations during the winter presumably in response to marine aerosol inputs. As with most other parameters, magnesium dynamics in the Mersey River exhibit some lag effects with maxima being recorded during January and February and minima observed during April.

Sulphate

In areas underlain by Devonian granites such as in Kejimkujik National Park, the major source of sulphate is expected to be from the atmospheric deposition of marine and anthropogenic sulphur compounds. Although natural geological sources such as the weathering of mineralized slates or gypsum may also contribute sulphate, they appear to represent a small percentage of the total sulphate load. Gridley (1987) has indicated that the Kejimkujik area has a low to moderate risk of natural mineral acid from the weathering of mineralized slates. Furthermore, mass budgets for the Mersey River (Figure 42) and Moosepit Brook (Figure 43) during 1984 indicated that approximately 75% of the river sulphate flux can be accounted for by wet sulphate deposition. Given an estimated dry deposition of approximately 20% of the wet deposition, it appears that terrestrial sulphate sources are of minor importance.

Seasonal patterns of sulphate concentrations in the various order systems are presented in Figures 44 to 47. With the exception of the well at Pebbleloggitch Lake (Figure 48), all sites exhibit very similar seasonal dynamics with the highest concentrations occuring during December to February and the minima observed from June to September. The only other parameters which exhibit seasonal dynamics that are nearly identical in all systems are sodium and chloride which like sulphate are predominately dependent on atmospheric supply. However the early winter peaks in

sulphate concentrations and fluxes do not correspond to periods of high wet precipitation sulphate concentrations or deposition. Although river flux and atmospheric wet deposition of sulphate agree on an annual basis, they exhibit vastly different seasonal dynamics. Atmospheric sulphate deposition is event specific and has no obvious seasonal pattern. However, river sulphate flux, regardless of system order, peaks during the winter and early spring and reaches a minimum during the late summer and early fall. This indicates that although the Kejimkujik watersheds do not have significant sulphate sources, they do play an active role in seasonal dynamics and subsequent delivery of sulphate to receiving waters.

Although the mechanisms controlling sulphur cycling within the organic systems are not well understood, it is possible to make some observations from the seasonal plots. In the first order streams the sulphate minima occur during the summer months, even though sulphate concentrations in precipitation tend to be elevated. These sulphate minima correspond to periods of maximum DOC concentrations which suggests that the sulphur compounds during this period may be accumulated as organic sulphur or as sulphate absorbed to organic compounds. Similar observations have been made by Likens et.al. (1977) and Dovland and Semb (1978).

Skartveit (1980) observed that sulphate concentrations in runoff from Breidvikdalen were affected by biological activity with the high values observed during periods of vegetative dormancy.

The Kejimkujik streams also exhibit elevated sulphate concentrations during the late fall and winter, with the peak values coinciding with the DOC minima. One possible explanation for this pattern is that there is some release of organic sulphur and absorbed sulphate as the vegetation senesces and the organic matter oxidizes. The relatively good agreement between the annual atmospheric deposition and the river flux of sulphate indicates that storage of sulphate in the basin is a short term process and that a seasonal storage and release mechanism is indeed in operation. Figure 49 presents monthly estimates of export and wet deposition of sulphate for Moose Pit Brook and indicates that there is sulphate retention during May to November and a net loss during December to April. Another potential mechanism which may be involved in the elevation of sulphate concentrations in these basins is that during the late fall and early winter, increased discharge and freezing of the soil profile limits the interaction between precipitation and the terrestrial basin. This process lessens the potential of sulphate reduction and storage. Although both of these mechanisms are without doubt involved in the elevation of sulphate concentrations during the winter, the relative importance and timing of each process is unknown. The higher order systems such as the Mersey River exhibit similar sulphate seasonal dynamics but there is no apparent inverse relationship with DOC. In fact DOC concentrations in the Mersey River peak just slightly in advance of the sulphate maxima. Whether this is a consequence of seasonal damping due to the storage potential of this system or indicates differences in the

relative importance of the various mechanisms that can result in elevated sulphate is uncertain. At first glance, the fact that the higher order systems have higher minima than the first order streams would suggest that sulphate reduction and oxidation processes may be less important in systems such as the Mersey River. However, the monthly sulphate export estimates (Figure 50) indicate that the Mersey River retains sulphate from May to November and that during the summer period exports only slightly more sulphate per unit area than Moose Pit Brook. Given that the Mersey River has elevated summer sulphate concentrations and similar exports, there must be a concentration process which serves not only to increase concentrations but also to reduce discharge. One possibility is that the large storage reservoirs in higher order systems can result in increased evapo-transpiration which will in turn result in elevated concentrations and reduced flows relative to first order systems. Figure 51 presents the ratio of river runoff to precipitation amount and indicates that although both the Mersey River and Moose Pit Brook basins store water from May to January, the Mersey River consistently retains more of the incoming precipitation. Thus, it is possible that the higher summertime sulphate concentrations observed for the Mersey River are largely dependent on higher evapo-transpiration rates.

The water from Pebbleloggitch well has a very different seasonal pattern than was observed for the surface waters, with the maxima occuring during early fall and minima observed from January to March. This seasonal pattern is similar to the sulphate

seasonal dynamics in precipitation and is inversely related discharge. This suggests that the recharge water entering the groundwater aquifer has limited interaction with the terrestrial system and thus has sulphate concentrations that reflect atmospheric supply and hydrologic control of concentration and dilution processes. This lack of interaction with the terrestrial system is further supported by the fact that even though the well is situated at the shore of the highly organic Pebbleloggitch lake, the groundwater always exhibits very low DOC concentrations. In order to explain the observed differences in groundwater and surface water chemistry during periods of ground water discharge, it must be assumed that movement into the surface water system proceeds at a slow enough rate to enable interaction with the terrestrial system and subsequent biological and geochemical modification of the water chemistry.

Chemical Interactions

The previous sections have focussed on the seasonal dynamics of parameters associated with terrestrial weathering, marine aerosol and natural and anthropogenic acidification processes in aquatic systems in southwestern Nova Scotia. However, these sections have essentially considered each parameter separately rather than from a comprehensive geochemical perspective. This section will attempt through the use of graphics, multiple linear regression and principle component analysis to present an overall view of acidification in various order systems.

Figure 52 presents the seasonal variability of sulphate, DOC and pH for Moosepit Brook and indicates that the stream pH is relatively stable even though sulphate and DOC concentrations exhibit considerable seasonal variation. This figure suggests that pH in this system is under the control of both mineral and organic acids, being naturally acidified by organic acids during the summer and LRTAP acidified during the winter and spring. This dual control of pH is apparent for other headwater streams (Figures 53 and 54) and to a lesser extent streams draining headwater lakes (Figures 55 to 57) in this area and has previously been documented for Atkins Brook by Kerekes et. al. (1986). It should be noted that the observed seasonal sulphate dynamics are controlled by terrestrial processes rather than the seasonal pattern of atmospheric supply. Although sulphate deposition during the summer is significant, internal alkalinity generation due to sulphate

reduction and/or hydrogen and sulphate retention in the basin serve to ameliorate the mineral acid influence on surface waters. The subsequent release of the retained sulphate and hydrogen ions during high flow periods results in enhanced surface water mineral acidification. Similar observations have been made by LaCroix and Townsend (1987) and Roussel et al. (1988). Thus the seasonal cycling of sulphate in these basins tends to concentrate the effects of the annual supply of mineral acids to a short time span during high flows. In the past, reduced vernal pH values in streams and lakes in Atlantic Canada have been attributed to the release of acidic compounds stored in the snowpack. Although this process is probably involved, snowmelt may also provide the increased discharge necessary to flush the stored mineral acids from the terrestrial basin into the receiving waters.

Although this dual control of pH is highly probable, it is also possible that during the winter there is still sufficient DOC in the system to provide organic buffering and thus the mineral acid additions will have little effect on the pH. In a situation where there is no organic buffering, the negative gran alkalinity should be equal to the hydrogen ion concentration as measured by pH electrode. Conversely, in situations where there is organic buffering, the negative Gran alkalinity will be much lower than the hydrogen ion concentration. Figure 58 presents the seasonal plot of the sum of Gran alkalinity and hydrogen ion concentration for Moosepit Brook and indicates that organic buffering is of minor importance during the winter and spring. Thus it appears that the

pH of Moosepit Brook is indeed under the control of both organic and mineral acids. This is particularly important with respect to the scenario of future emission reduction as it implies that the headwater systems will respond to reduced deposition and exhibit elevated winter and spring pH levels. Figure 59 presents the seasonal pattern of estimated percent composition of organic and mineral acids for Moosepit Brook. Using organic anion concentrations calculated from the empirical relationship of Oliver et al. (198) indicates that there is nearly complete organic acid domination during the summer and an equal organic and mineral acid mixture during the winter. However, if the organic anion concentration is estimated by the difference in the ion balance (Σcations - Σanions), approximately 80% of acidification is estimated to be due to strong mineral acids.

The higher order Mersey River has a very different seasonal pattern as is indicated by Figure 60. The pH tends to exhibit more pronounced seasonal variation than is observed for the first order streams with the lowest values occuring during the winter and the maxima during the summer and fall. The periods of low pH tend to occur during periods of high sulphate concentration and to a lesser extent high DOC concentration. The maximum pH levels coincide with the sulphate minima but not necessarily the lowest DOC concentrations. This suggests that the pH of the Mersey River is to a great extent a function of the strong mineral acid concentration. A similar pattern is observed for Little River (Figure 61). Figure 62 shows the seasonal pattern of the relative

contribution of organic and mineral acids for the Mersey River. Although this pattern is similar to that observed for Moose Pit Brook, it is readily apparent that mineral acidity is important throughout the entire year, not just during the winter.

Multiple linear regression analysis between hydrogen ion concentration and several water quality parameters (DOC, SO_4, NO_3, Silica, Cl, K, Ca, Discharge) was attempted for two data sets but significant relationships were observed only for the Mersey River. Results of this regression analysis are presented in Table and indicates that $[H^+]$ is positively related to discharge, sulphate and nitrate concentrations. This result further supports the observation that changes in Mersey River pH are more strongly dependent on changes in mineral acidity than natural organic acidity.

In an attempt to get an appreciation of the processes controlling water quality variability principal components analyses were performed on these two data sets. The results of these analyses are summarized in Figure 63 and for the sake of clarity only consider parameters which have correlation co-efficients greater than 0.32. The first principal component is similar for both systems in that it explains 39 percent of the variation and includes parameters which are associated with terrestrial weathering and marine aerosol influence. It is interesting to note that silica is only observed in the principle component for Moosepit Brook which may indicate greater influence of groundwater

in the headwater basin. The second principle component is also similar for the two systems and explains approximately 24% of the variation in the data. This component exhibits high weightings for those parameters associated with mineral acidity and indicates that LRTAP acidification is an important process in both first and higher order systems in southwestern Nova Scotia. Discharge is an important variable in the Mersey River principle component and indicates that atmospheric processes can only be important when there is sufficient discharge to overcome the large water storage potential of this basin.

The third principle component explains essentially equal percentages of variation (≈ 14%) but it appears to represent different processes for the two systems. At Moosepit Brook, DOC and hydrogen are negatively weighted while sulphate and chloride are positively weighted. This appears to indicate periods of high organic acidity associated with low atmospheric inputs of marine and anthropogenically derived anions. However it should be noted that both sulphate and chloride can be taken up or stored by vegetation and thus there may be a more direct biochemical linkage between DOC and these anions. Thus, as was apparent from Figure 59, mineral and organic acidification processes are both important at Moose Pit Brook. The third principle component for the Mersey River is also negatively weighted for DOC but hydrogen ion is not a significant contributor and thus this component is not indicative of organic acidity. Both chloride and potassium are positively weighted which may indicate low marine influence during periods of

high DOC supply. However it should be noted that both potassium and chloride are the dominant salts in plant tissues and thus this component may relate to the vegetative cycling of DOC, chloride and potassium. Regardless of the interpretation of this principle component it is readily obvious that organic acidity is not a dominant process in this higher order system.

In order to investigate whether or not there is any meaningful ordination of the data by season, the principle component scores for the two systems were plotted. Figures 64 to 66 present scatterplots of component scores of the first principle component (PC 1) versus the second principle component (PC 2) for Moosepit Brook and the Mersey river respectively. Figure 64 indicates that for Moosepit Brook weathering processes dominate during the autumn while mineral acidity is the most extensive during the first four months of the calendar year. In addition during periods when mineral acidity is dominant, weathering processes are at a minimum and vice versa. Figure 65 indicates a slightly different monthly ordination for the Mersey River. The dominance of mineral acidity exhibits a much more restricted seasonal component occuring during the month of March. The greatest terrestrial weathering occurs later than that observed for Moosepit Brook, spanning the autumn and early winter. In addition the highest mineral acidity occurs during periods of moderate terrestrial weathering instead of during minimum weathering. This less distinct seasonal ordination of the Mersey River components is undoubtedly a consequence of the large storage capacity of the Mersey River which tends to damp seasonal

variability. Also, as atmospheric inputs can influence the Mersey River water chemistry only during periods of extreme discharge the very distinct winter peak of mineral acid dominance is to be expected.

Figure 66 presents a scatterplot of the scores from principle component 2 versus component 3 for Moose Pit Brook. From January to March, the parameters associated with LRTAP dominate the water quality while during the summer and fall the organic acidity component is at a maximum. In addition, when the mineral acidity component reaches a maximum, organic acidity is at a minimum and vice versa. Thus as Figure suggests, the principle component analysis indicates that both mineral and organic acidification processes are important determinates of the pH of first order streams in southwestern Nova Scotia.

CONCLUSIONS

The seasonal dynamics of selected water quality parameters from aquatic systems of varying hydrologic order located in southwestern Nova Scotia have been considered. Parameters which are predominately derived from terrestrial weathering (DOC, silica, calcium and magnesium) behave similarly, with seasonal patterns being related to system order. The first order streams and the streams draining headwater lakes exhibit maximum concentrations during the late summer and early fall and have minima from February to April. Although these patterns are inversely related to discharge, the relationships are relatively weak as biological and geochemical processes are also determinants of surface water concentrations. In addition, elevated concentrations are generally associated with discharge pulses during periods of low flow which indicates that there is a minimum flow required to flush terrestrially derived chemicals into the surface water systems. The higher order systems and the headwater lakes exhibit varying response lags and considerably reduced seasonal variability. The most extreme time lag ($\sim$ 3 months) is observed for the Mersey River which reaches a maximum during December and January and has minimum concentrations during April and May. These systems also exhibit elevated concentrations during periods of low flow.

Sodium and chloride in surface waters in Atlantic Canada are considered to be predominately of marine origin and thus a good balance between deposition and flux is to be expected. However,

wet deposition of sodium and chloride only accounts for approximately 30 percent of river export, which suggests that dry deposition is the dominant delivery mechanism for marine salts in this region. The seasonal pattern of sodium and chloride concentrations were similar in all systems, regardless of hydrologic order, and were markedly different from the patterns observed for the terrestrially derived parameters. The sodium and chloride maxima are observed during January and February and the minimum values occur during April to June. All systems had secondary peaks during October and November, but these were particularly pronounced in the lower order systems. As was noted for the terrestrially derived parameters, peak concentrations were associated with discharge pulses which suggests that either inwash of dry deposited marine salts or some terrestrial cycling of sodium and chloride is involved.

Annual deposition (wet and dry) of sulphate is very similar to river export which indicates that sulphate in the Kejimkujik systems is almost entirely derived from the atmosphere. However, the seasonal pattern of sulphate concentration and flux in precipitation is very different from that observed in the surface waters. Monthly loading estimates indicate that the Kejimkujik systems are retaining sulphate from May to November and losing sulphate during December to April. Thus, on a seasonal basis, the terrestrial basins appear to play an active role in seasonal dynamics and subsequent delivery of sulphate to receiving waters. All the systems considered exhibit very similar seasonal patterns,

with sulphate concentrations peaking during the winter and early spring and reaching a minimum during the late summer and early fall. Although the streams all exhibit nearly identical maximum sulphate concentrations, the higher order systems tend to have much higher minimum values than the first order streams. However, from the estimates of mass export and water balance, it appears that the differences in minimum sulphate concentration are largely due to greater evapotranspiration in the higher order systems.

The first order streams exhibit strong interactions between organic and mineral acids with basically an inverse relationship between sulphate and DOC concentrations. Organic acidity dominates during the summer and fall while mineral acidity dominates during the winter and spring. Thus acidification of these first order systems appears to be under dual control of both mineral and organic acidity. The importance of both mineral and organic acidity is emphasized by the fact that pH remains relatively stable despite the rather significant seasonal changes in DOC and sulphate concentrations. Principle component analysis for Moose Pit Brook confirms this dual control of the acidification process, with hydrogen and sulphate concentrations being highly weighted in component 2 and hydrogen and DOC concentrations dominating component 3. Mineral acidity dominates these systems during periods of sensitive lifestages for many species and thus LRTAP may result in detrimental biological responses even in highly organic waters. In the higher order systems DOC concentrations peak only slightly in advance of sulphate and thus the dual control of the

acidification process is not readily apparent. The seasonal pattern of pH is rather stable and tends to respond more readily to changes in sulphate than in DOC concentration. Multiple linear regression analysis for the Mersey River data set indicates that there is a good relationship between pH and sulphate and nitrate-nitrite concentration and that DOC concentration is statistically insignificant. Similarly principle component analysis indicates strong weightings for hydrogen and sulphate concentrations in component 2 and no components which were heavily weighted for hydrogen and DOC concentrations. As these higher order systems have lower concentrations of DOC and carbon pools which due to long system residence are probably dominated by refractory carbon compounds, mineral acidification can be expected to be an extremely important process. Contrary to what is observed in the first order streams, mineral acidification is a significant process throughout the entire year.

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ACKNOWLEDGEMENTS

The data used in this report represent the collective efforts of many agencies involved in acid rain studies at Kejimkujik National Park. Special thanks must go to the staff of the Water Quality Branch, Dr. J. Kerekes of Canadian Wildlife Service and Mr. F. Luxton who have been largely responsible for the establishement of high frequency long term data from these selected river systems. The author also appreciates the staff of the analytical laboratory of Water Quality Branch who are responsible for timely and reliable chemical analyses. I would also like to thank several people who reviewed and commented on the manuscript, particularily Dr. T. Pollock and Dr. A. El Shaarawi.

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PARAMETER	PARAMETER CODE
pH	10301
Specific Conductance	02041
Turbidity	02073
Water Colour	02011
Potassium	19103
Sodium	11103
Sulphate (Thorin; MTB; IC)	16303; 16304; 16309
Alkalinity (Total; Gran)	10101; 10110
Calcium	20110
Magnesium	12107
Chloride	17205; 17209
Aluminium	13305
Iron	26304
Manganese	25304
DOC	06107
Nitrate:Nitrite	07110

TABLE 1: CHEMICAL COMPOSITION OF BULK AND THROUGHFALL SAMPLES COLLECTED AT MOOSE PIT BROOK

STATION	DATE	pH	GRAN Alk.	SO_4 mg/L	Cl mg/L	Na mg/L	K mg/L	Ca mg/L	Mg mg/L
Sulk	08-Jun-87	4.6	-1.2	2.0	0.5	0.1	0.10	0.10	0.10
Throughfall	08-Jun-87	4.9	1.1	9.3	2.5	2.5	5.60	1.80	0.93
Bulk	15-Jun-87	6.5		4.6	0.5	0.1	0.10	2.40	0.10
Throughfall	15-Jun-87	4.9	0.5	9.3	1.3	1.9	3.90	0.97	0.48
Bulk	22-Jun-87	4.9	-0.5	0.9	0.5	0.1	0.15	0.10	0.10
Throughfall	22-Jun-87	4.9	0.3	2.5	2.6	1.3	3.30	0.65	0.31
Bulk	29-Jun-87	5.8	1.6	2.0	0.5	0.1	0.42	0.12	0.10
Throughfall	29-Jun-87	5.1	1.8	2.0	4.6	1.0	7.10	0.74	0.57
Bulk	06-Jul-87	3.7	-11.7	9.7	0.5	0.1	0.11	0.15	0.10
Throughfall	06-Jul-87	3.8	-8.9	6.1	13.8	2.1	8.50		

TABLE 3: RESULTS OF MULTIPLE LINEAR REGRESSION ANALYSIS BETWEEN HYDROGEN AND SELECTED WATER QUALITY PARAMETERS USING THE MERSEY RIVER DATA SET

		R^2	T	Overall F
H^+	NO_2-NO_3	.37	11.2*	317*
	log discharge	.66	17.3*	518*
	SO_4 (IC)	.72	20.2*	466*

$$H^+ = -.0069 + .207\ SO_4 IC + .066\ NO_2\text{-}NO_3 + .0085 \log \text{discharge}$$

$F = 466^*$ DF = 538 $R^2 = .722$ $SD_{REG} = .004$

* SL = .0001

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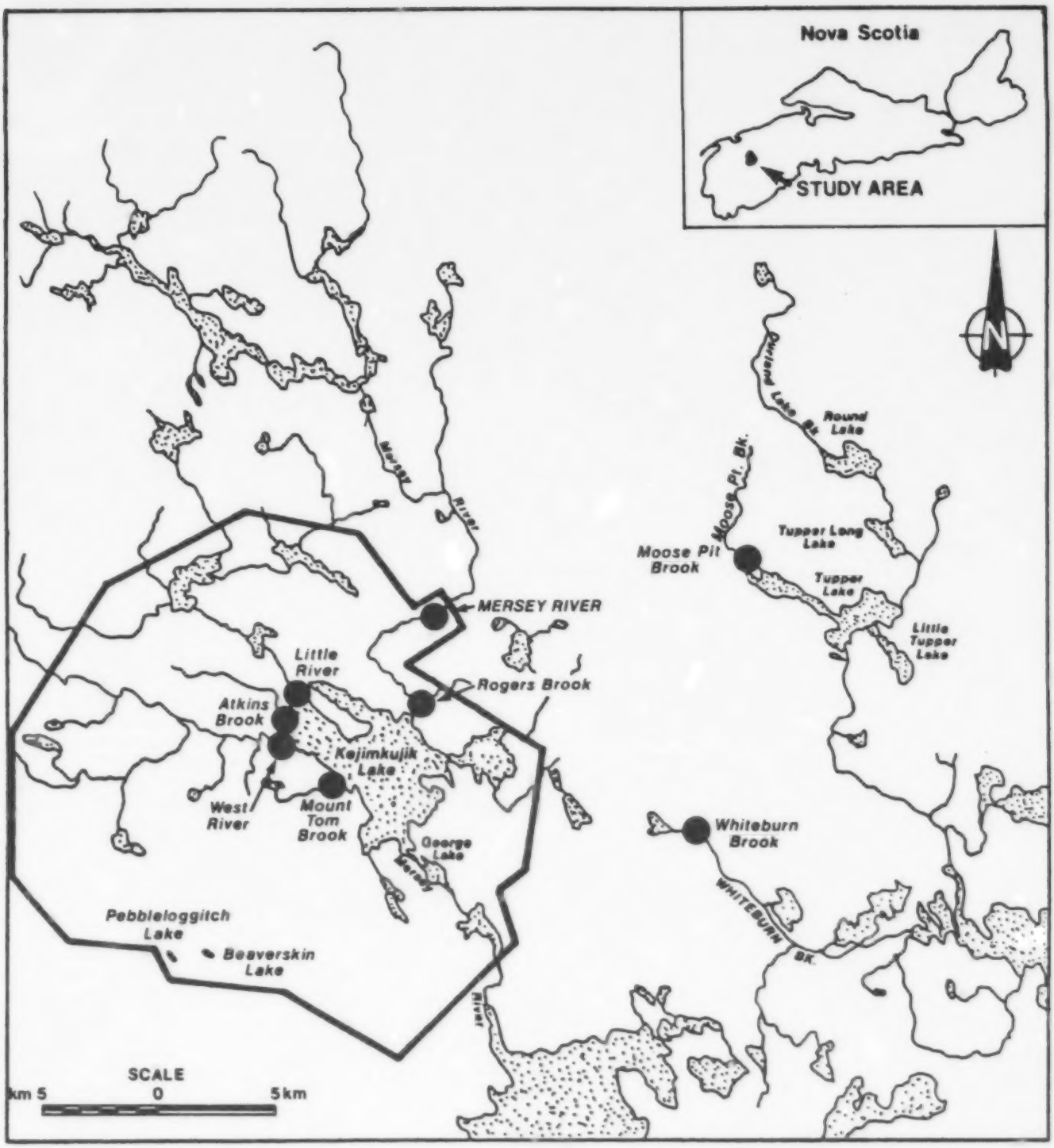

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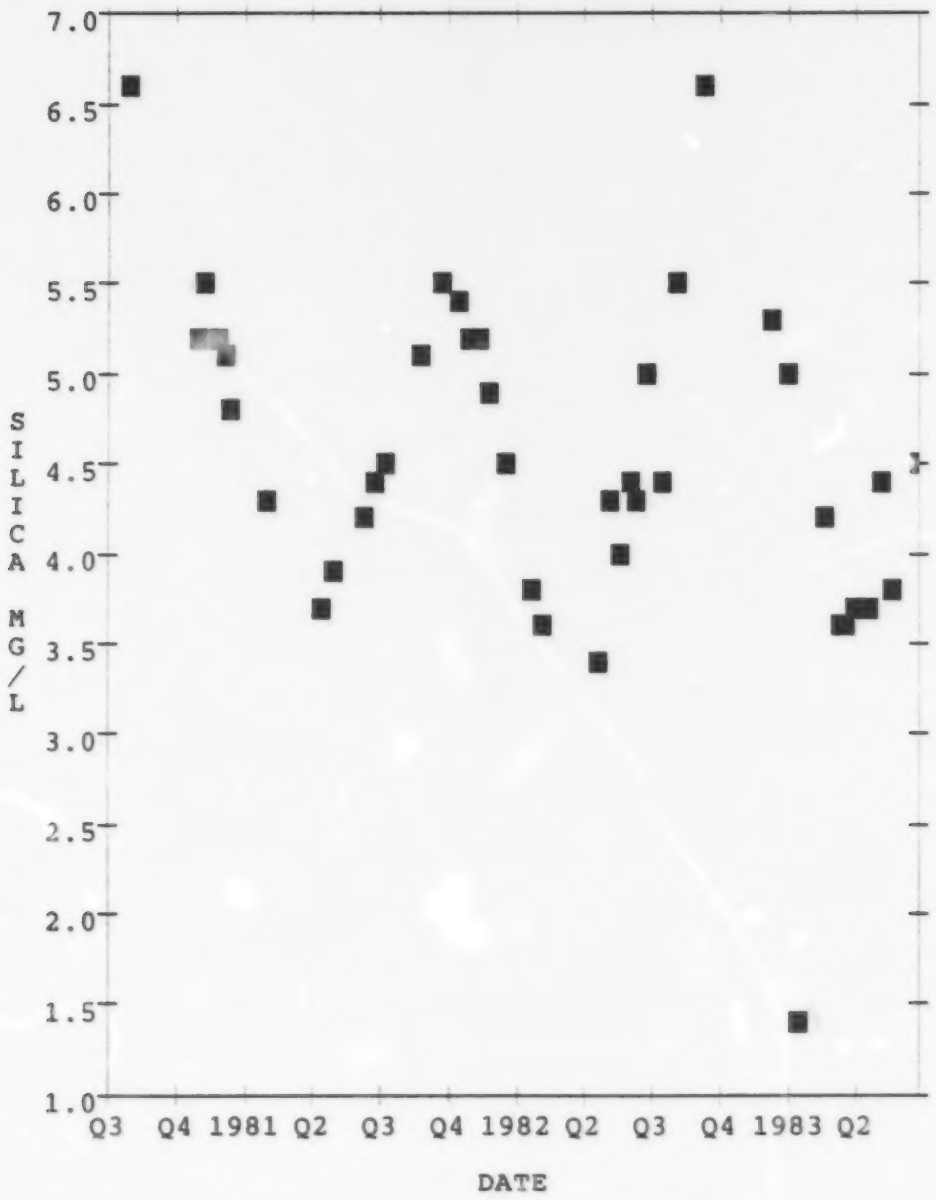

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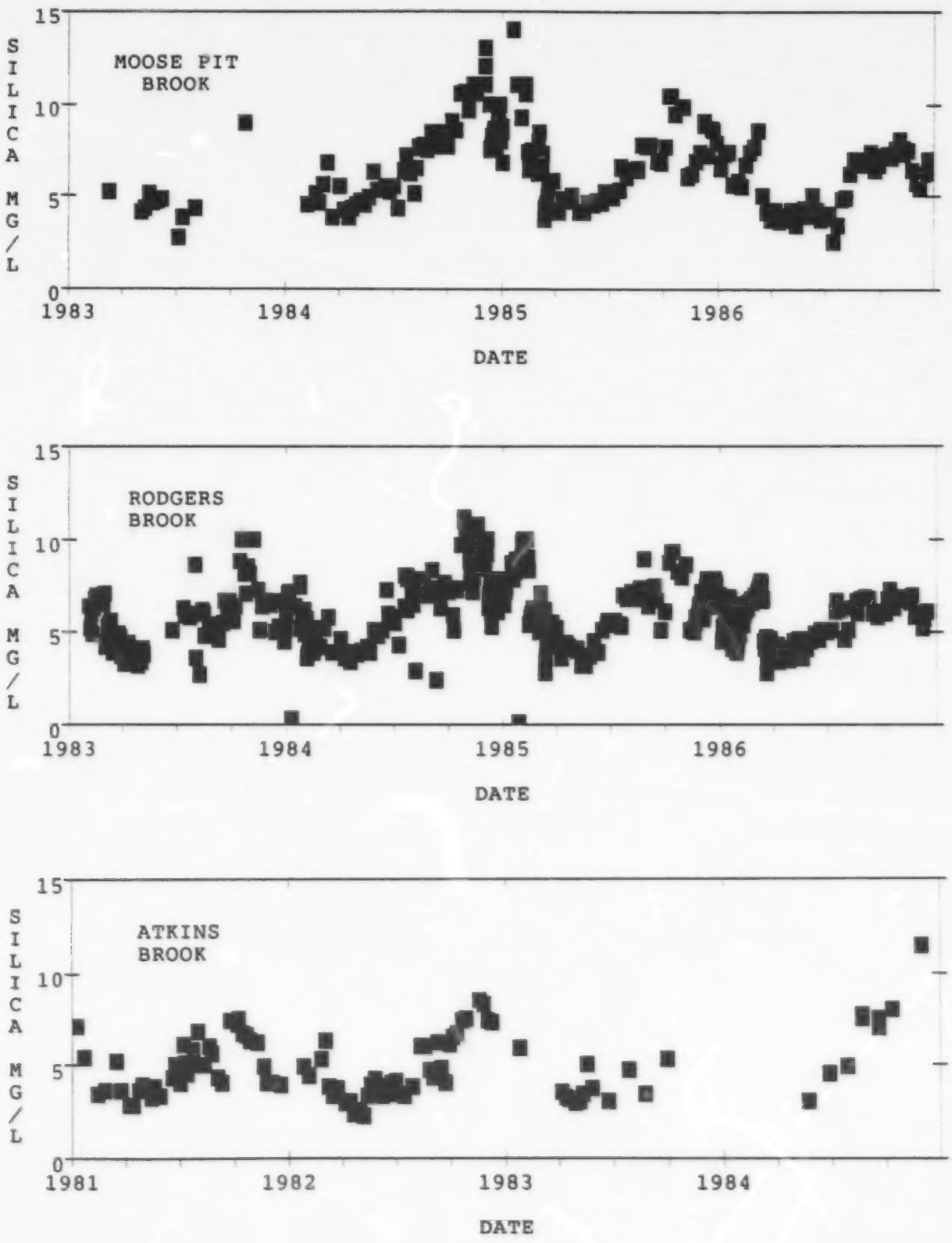

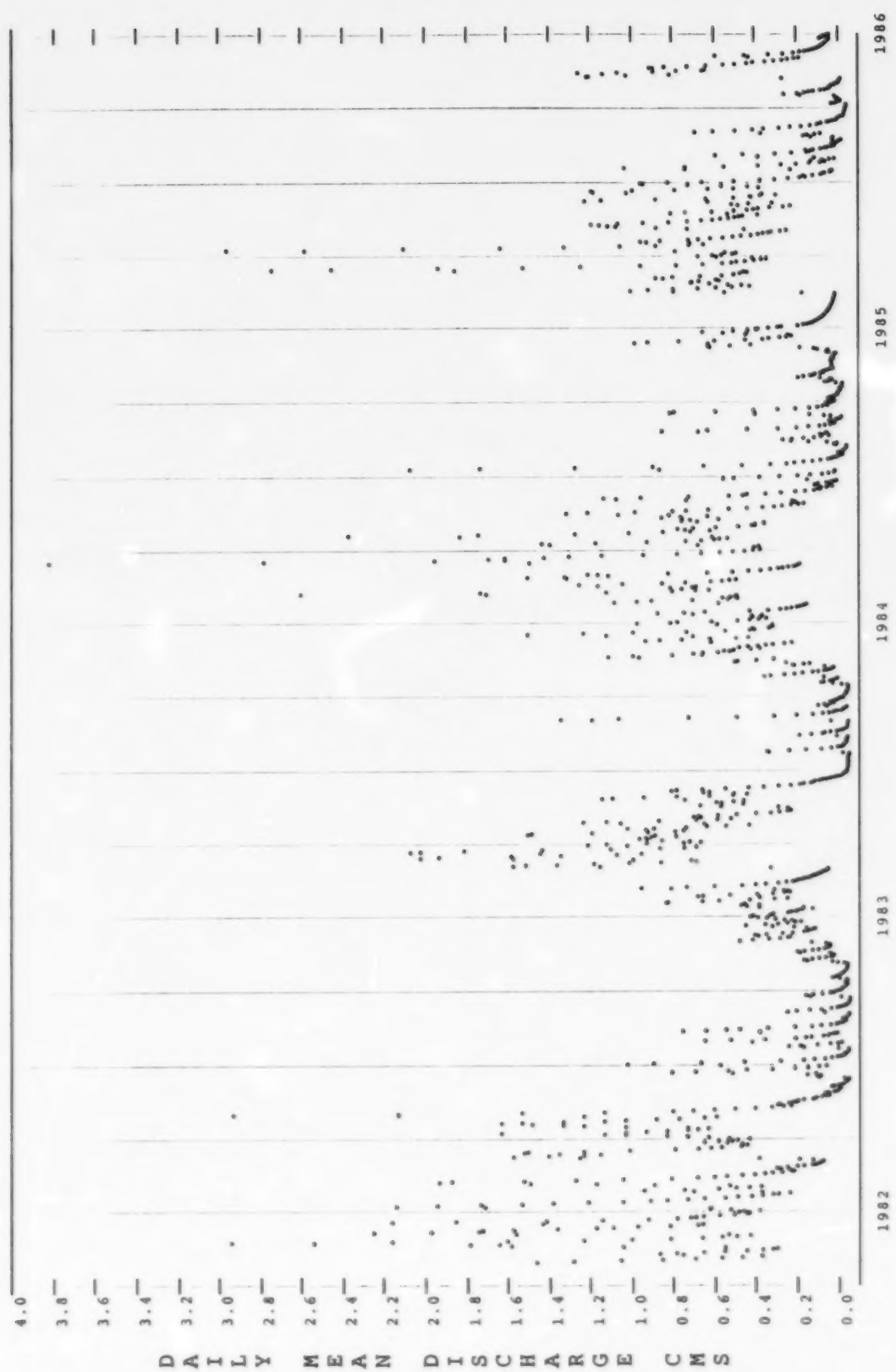

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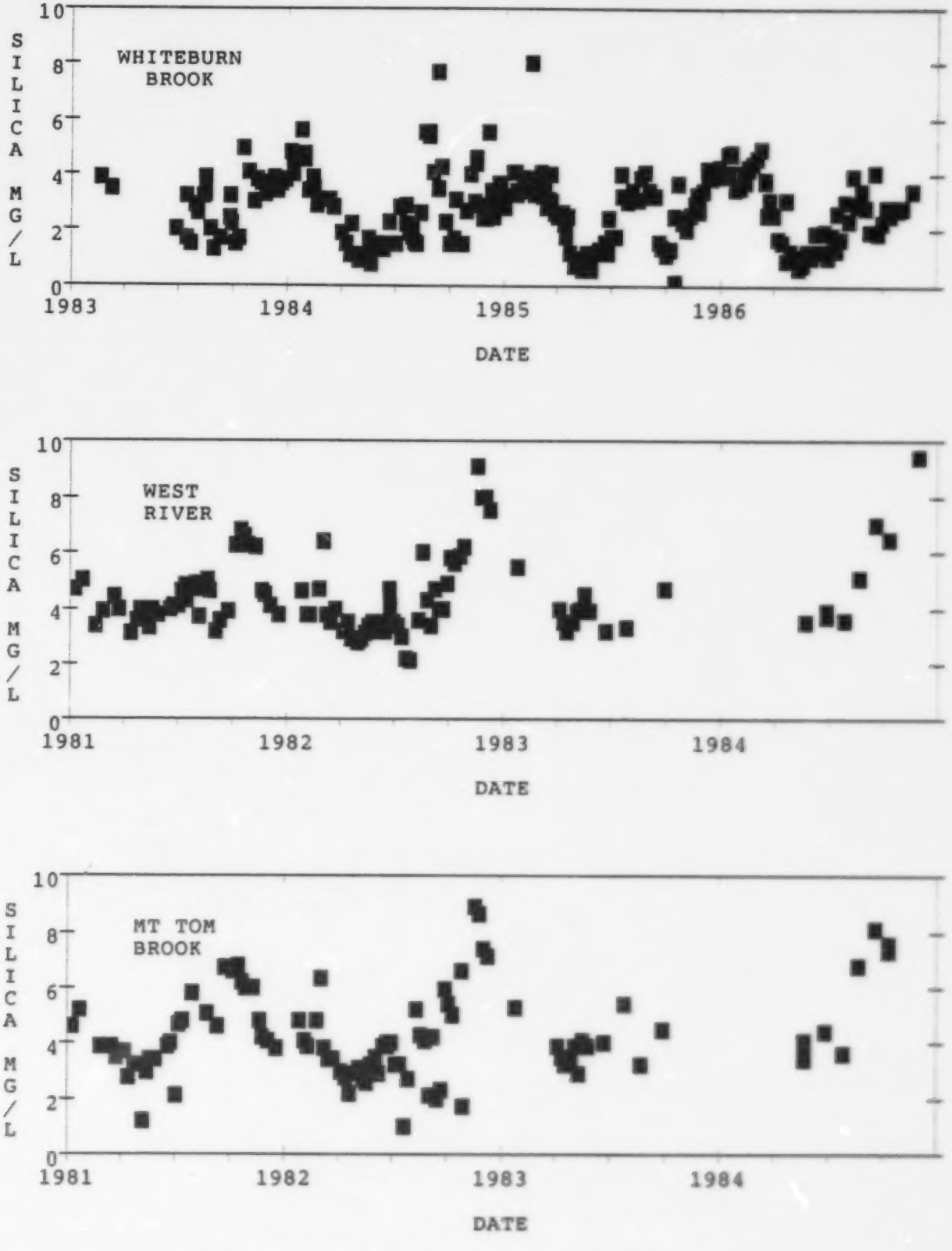

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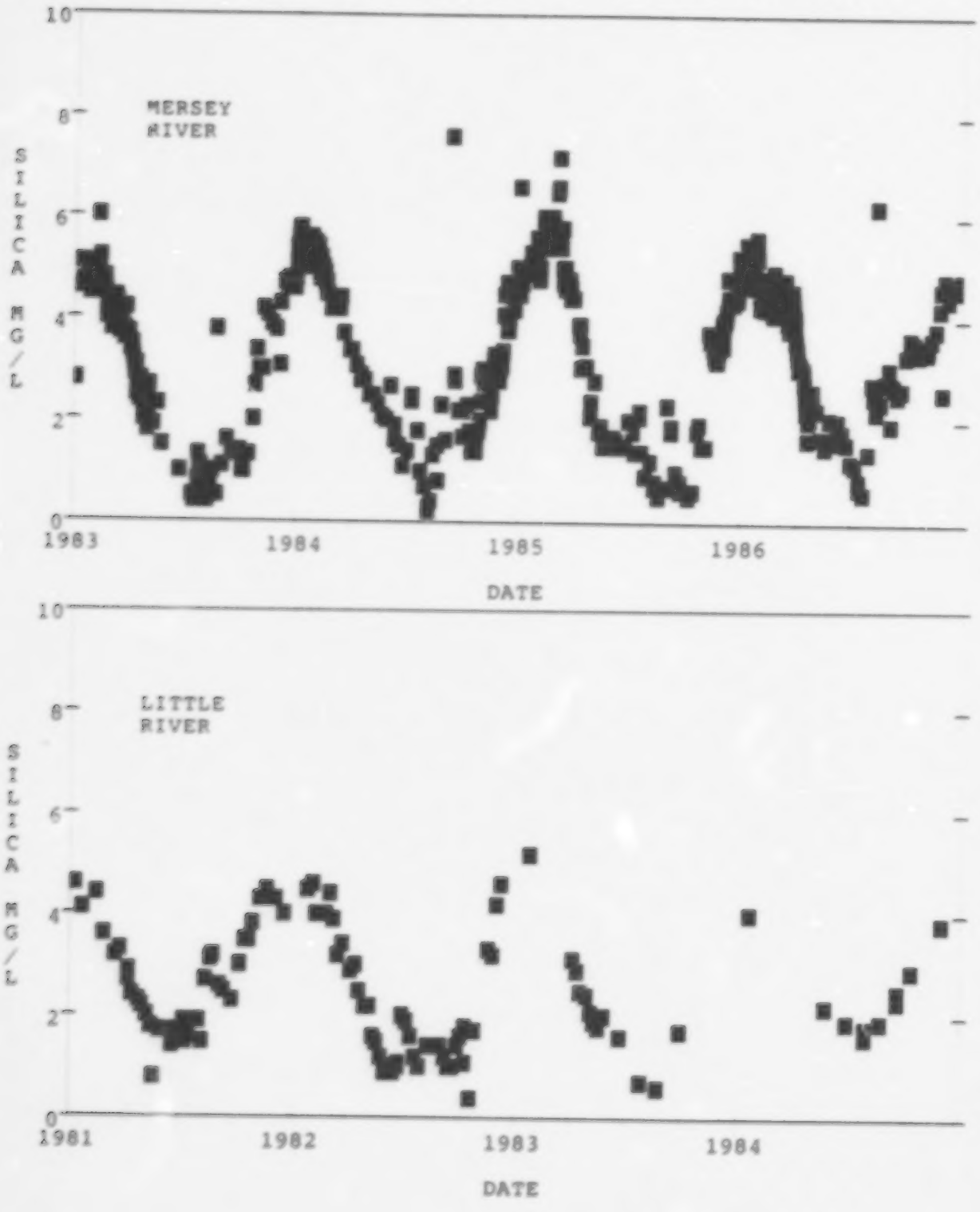
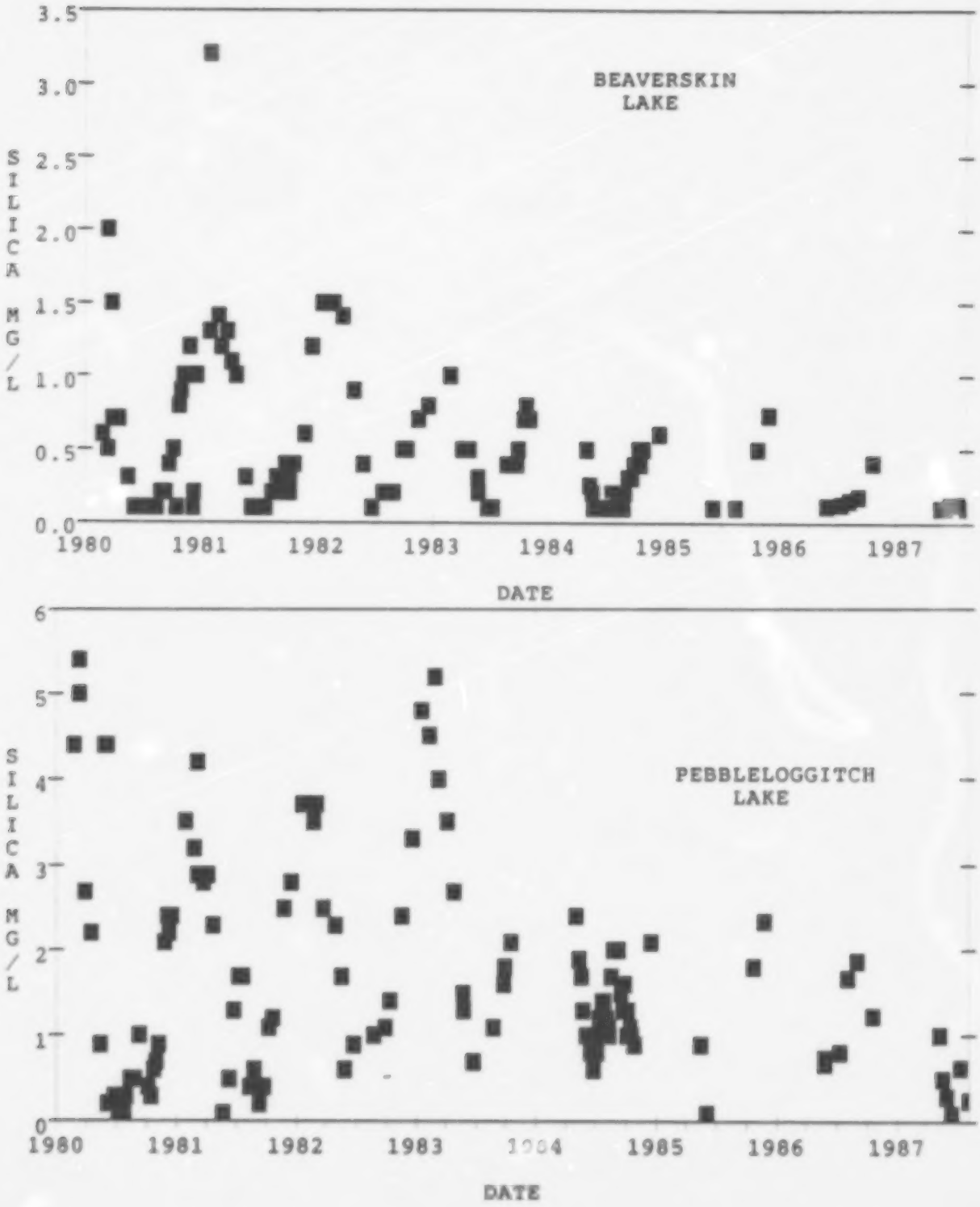
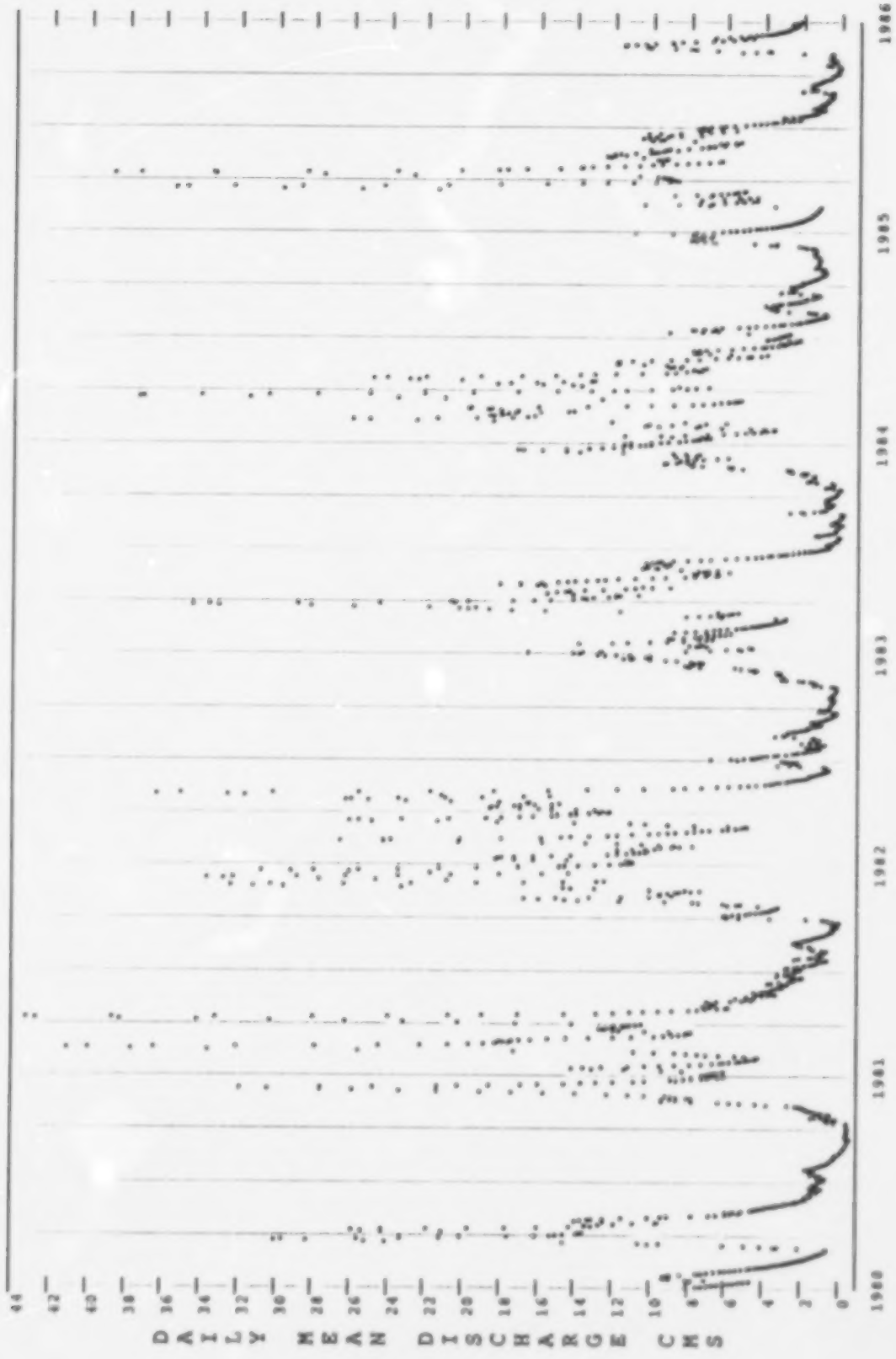


FIGURE 7: SILICA CONCENTRATIONS IN TWO HEADWATER LAKES





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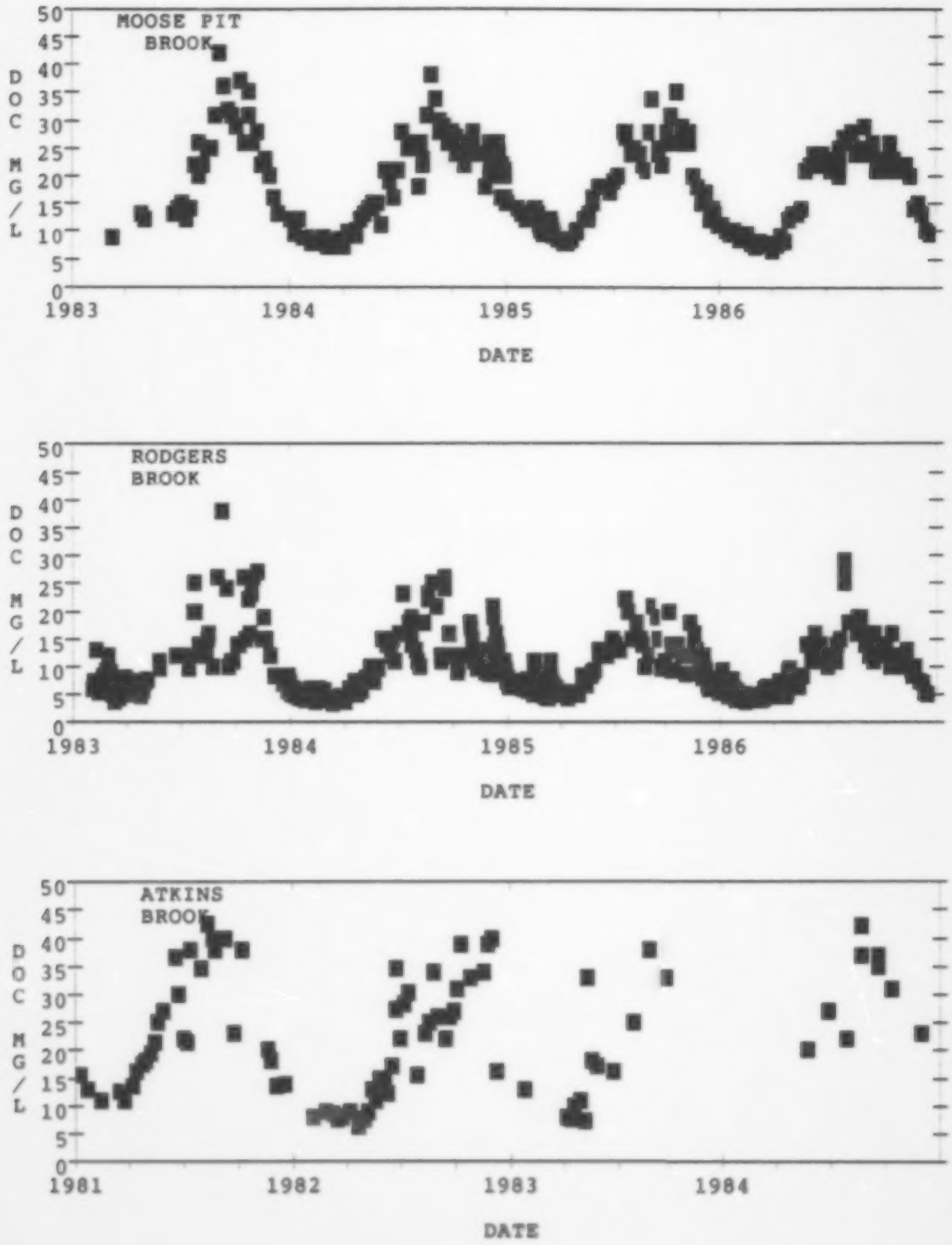

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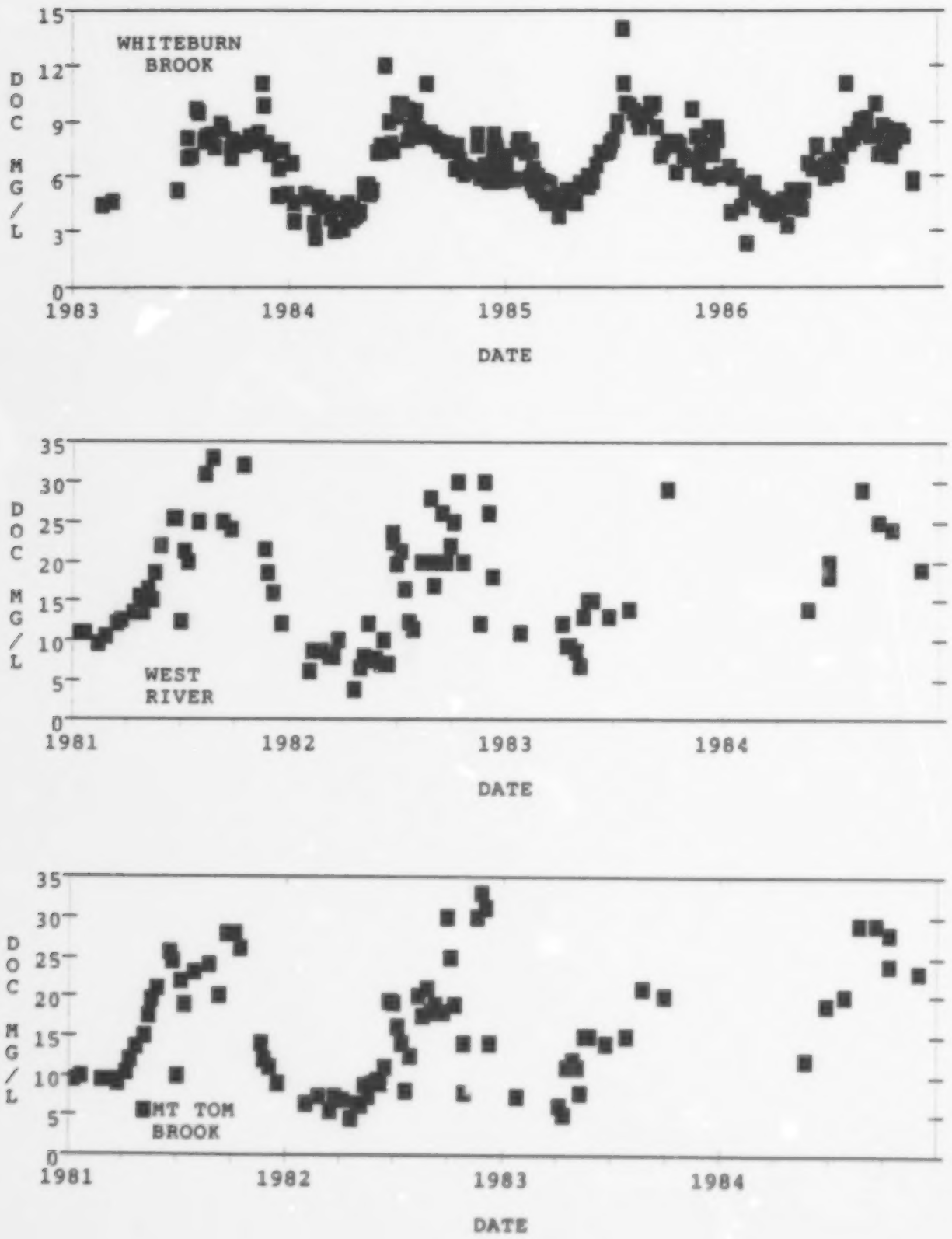

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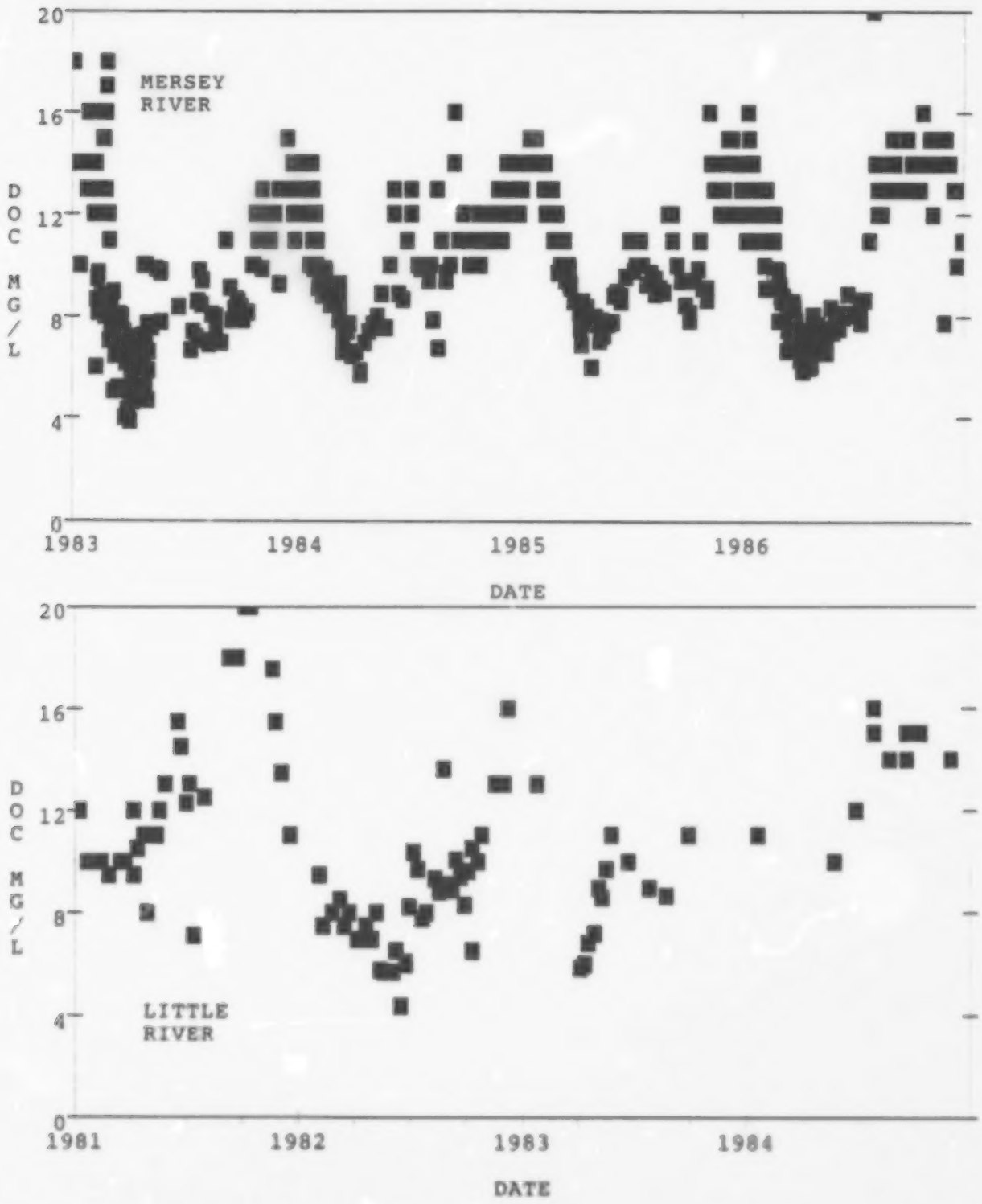
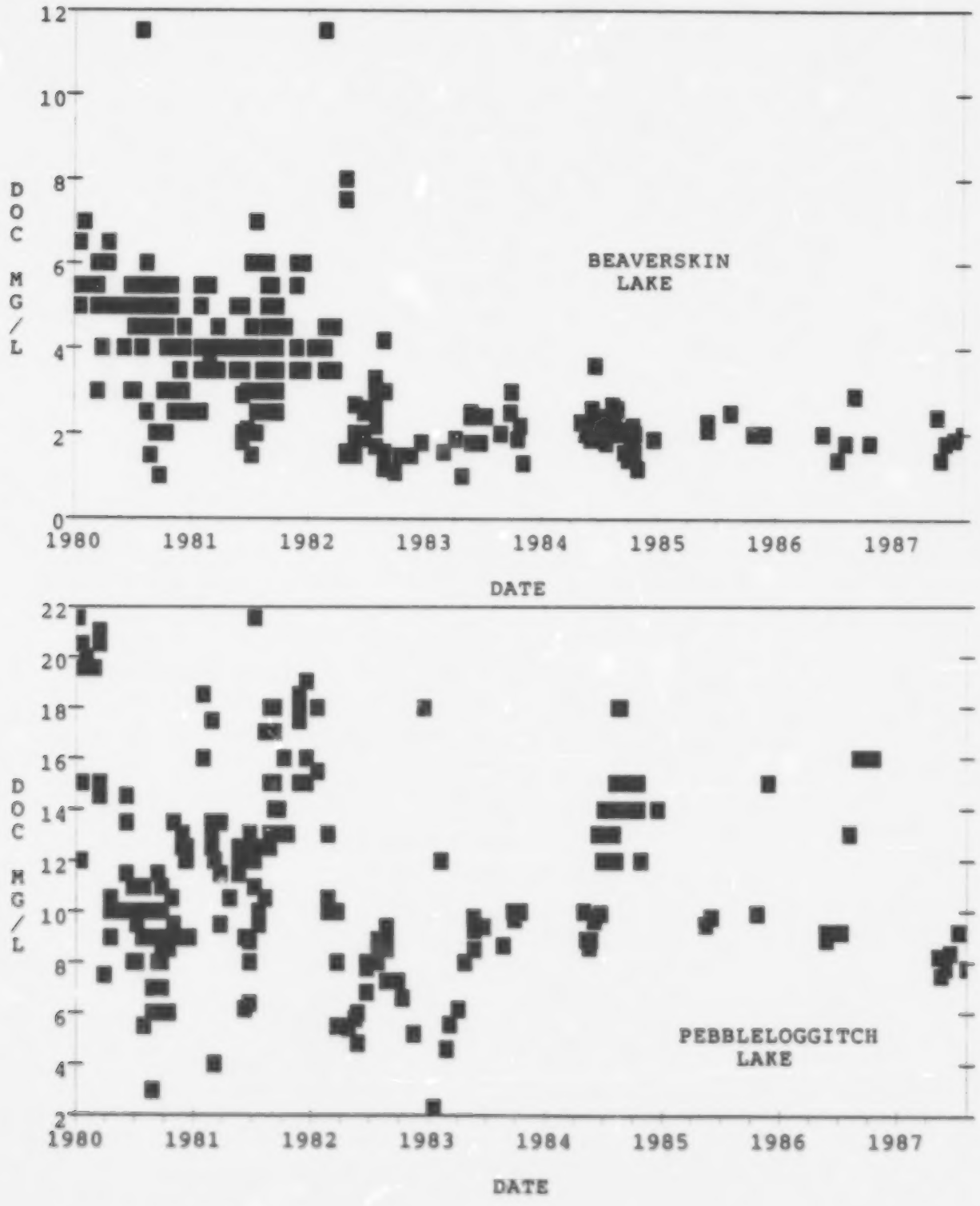


FIGURE 12: DISSOLVED ORGANIC CARBON CONCENTRATIONS IN TWO HEADWATER LAKES



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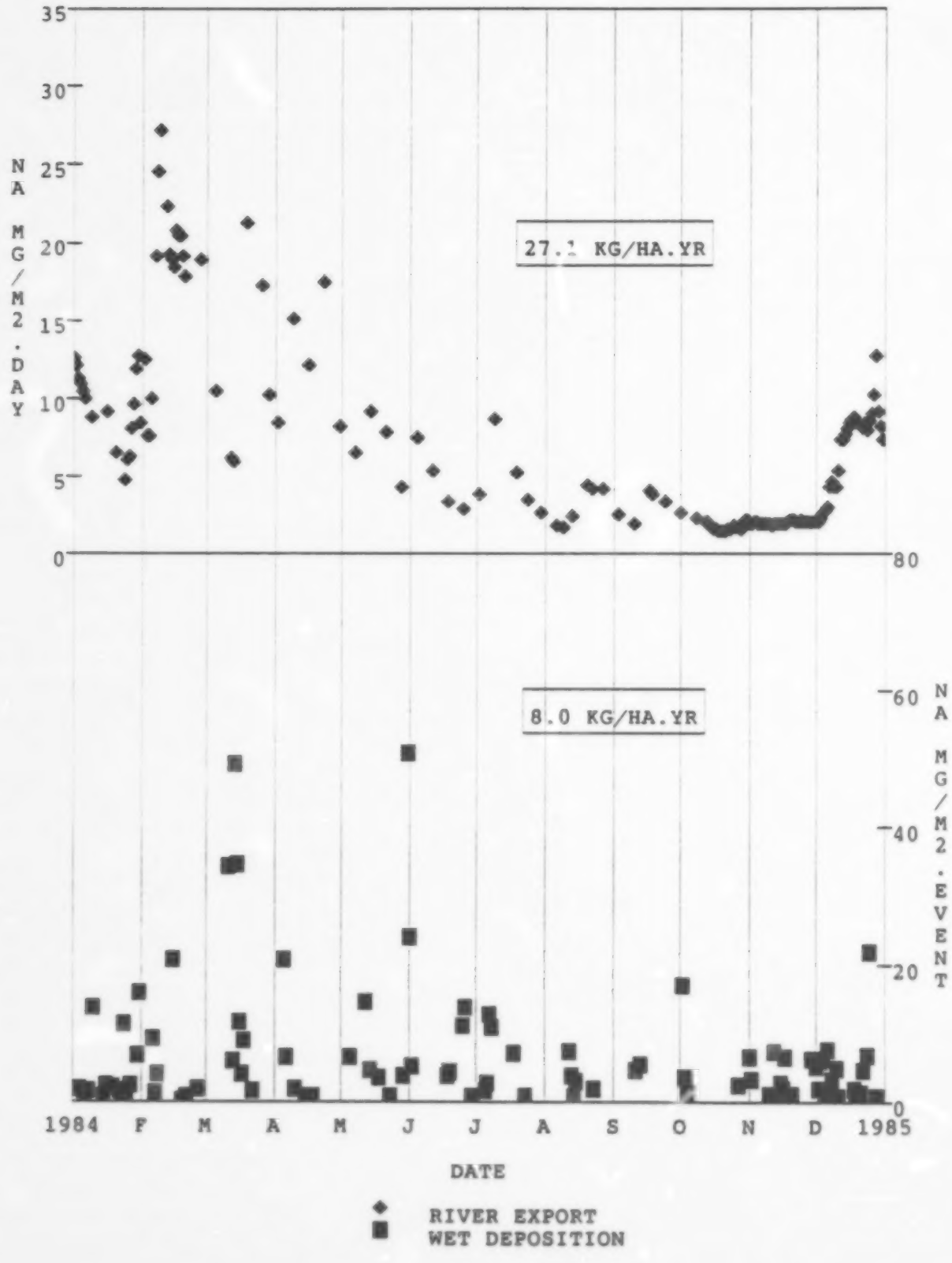

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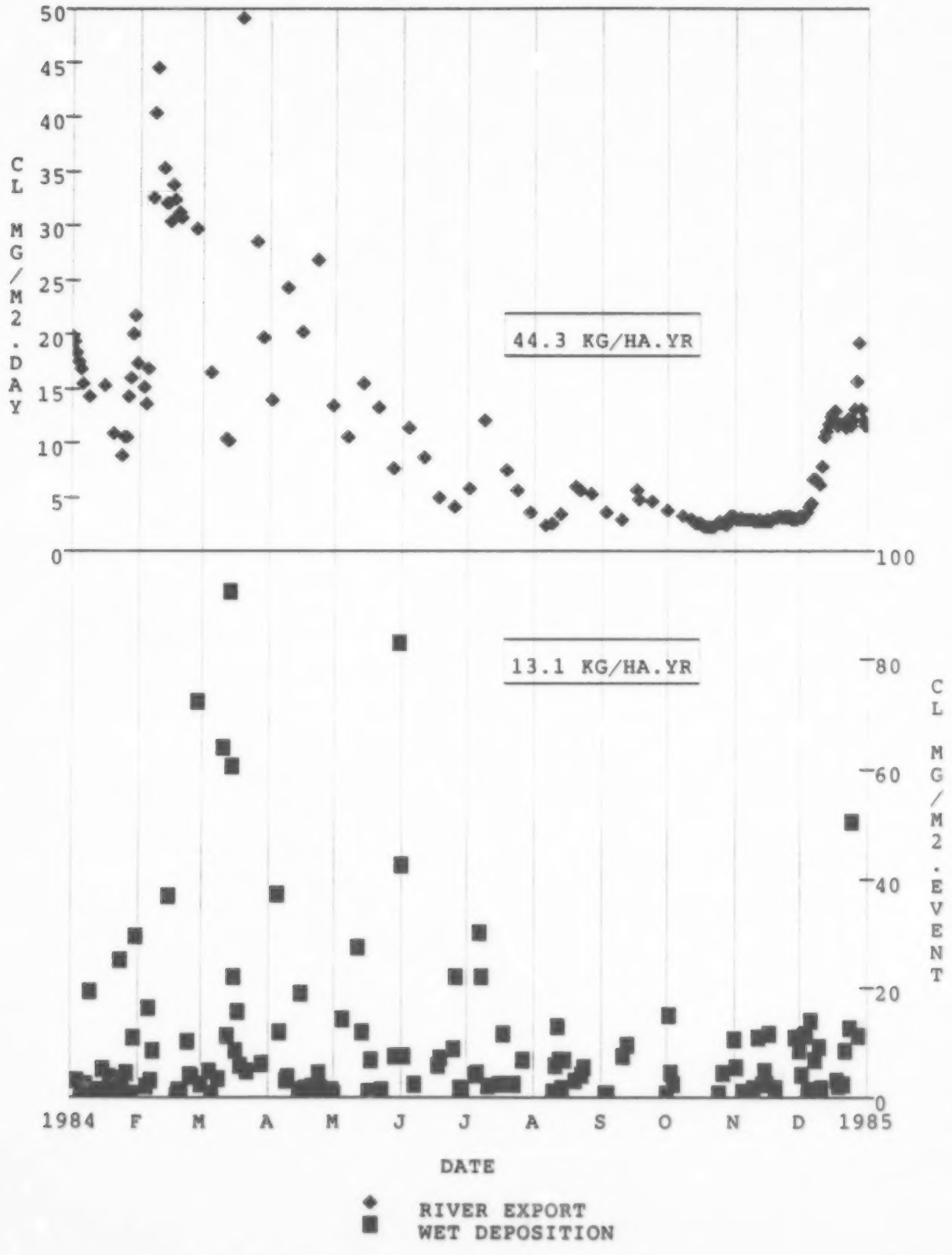

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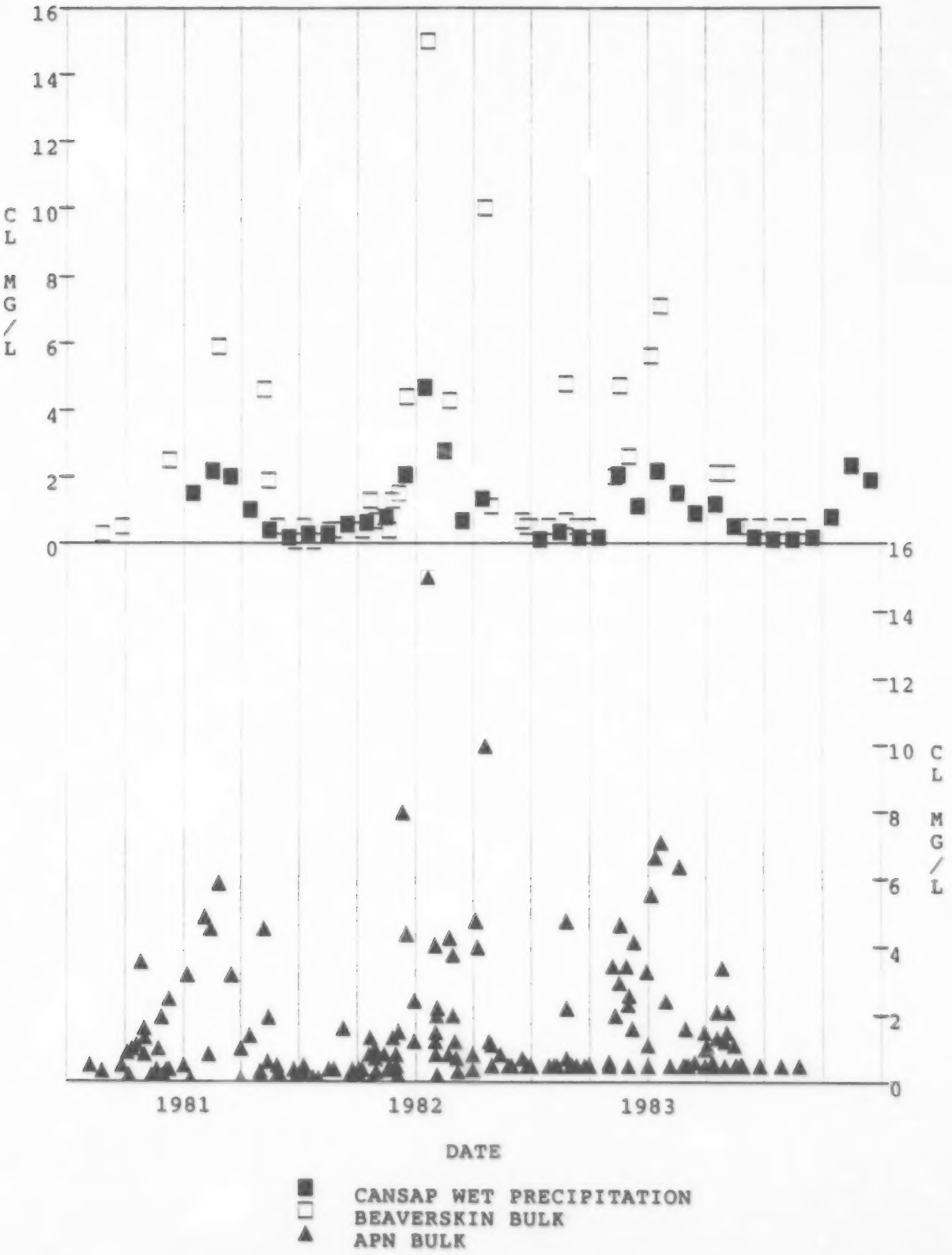

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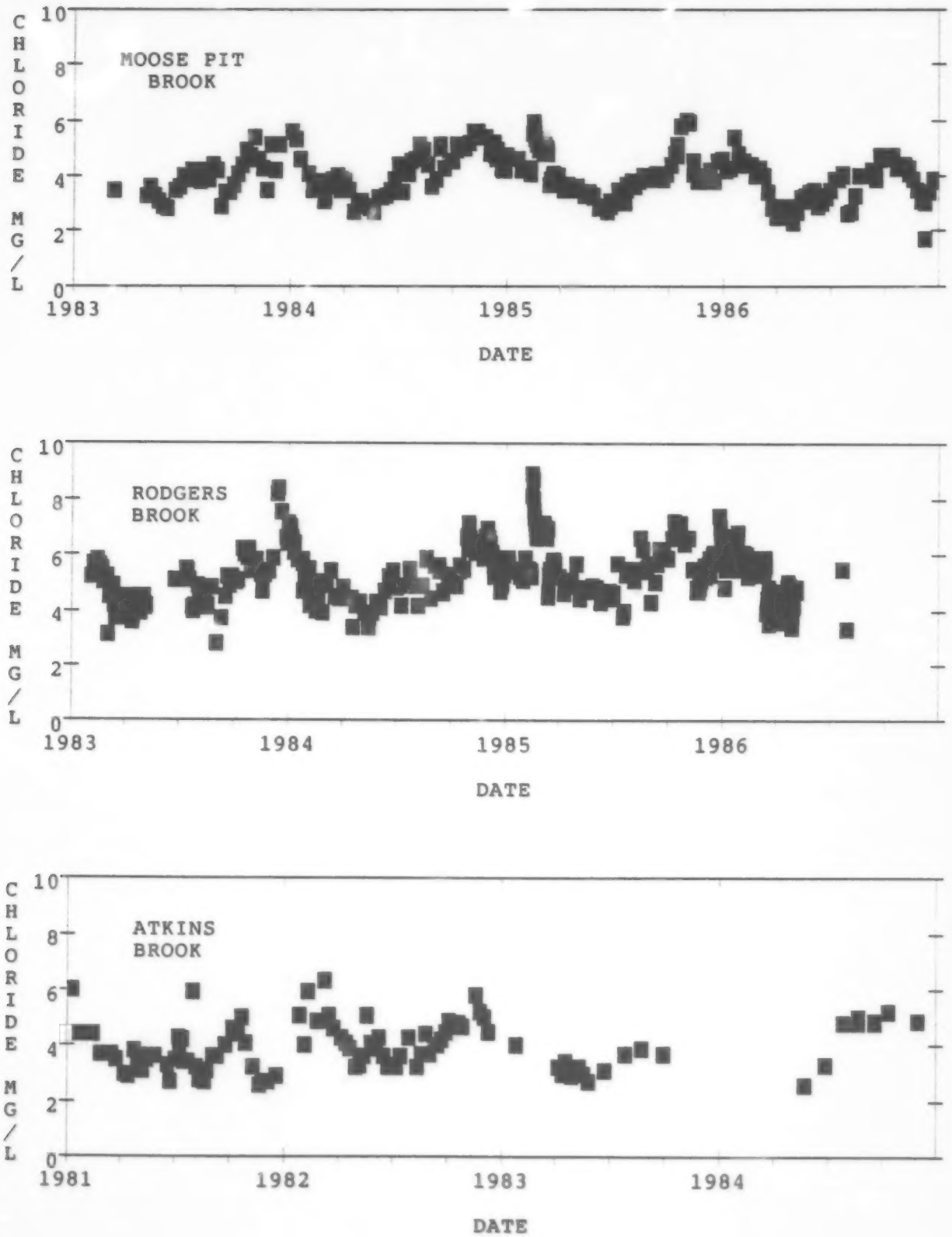

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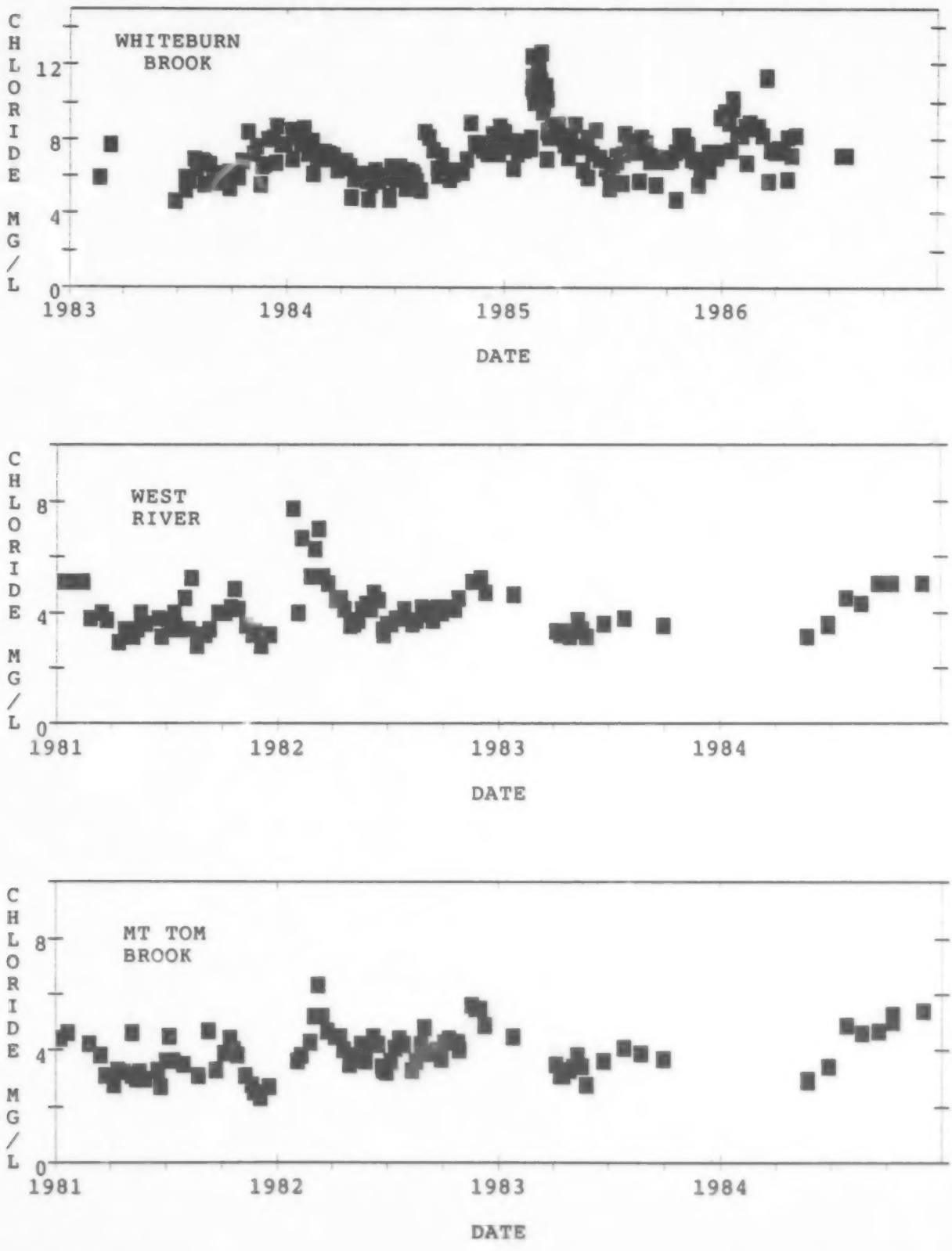

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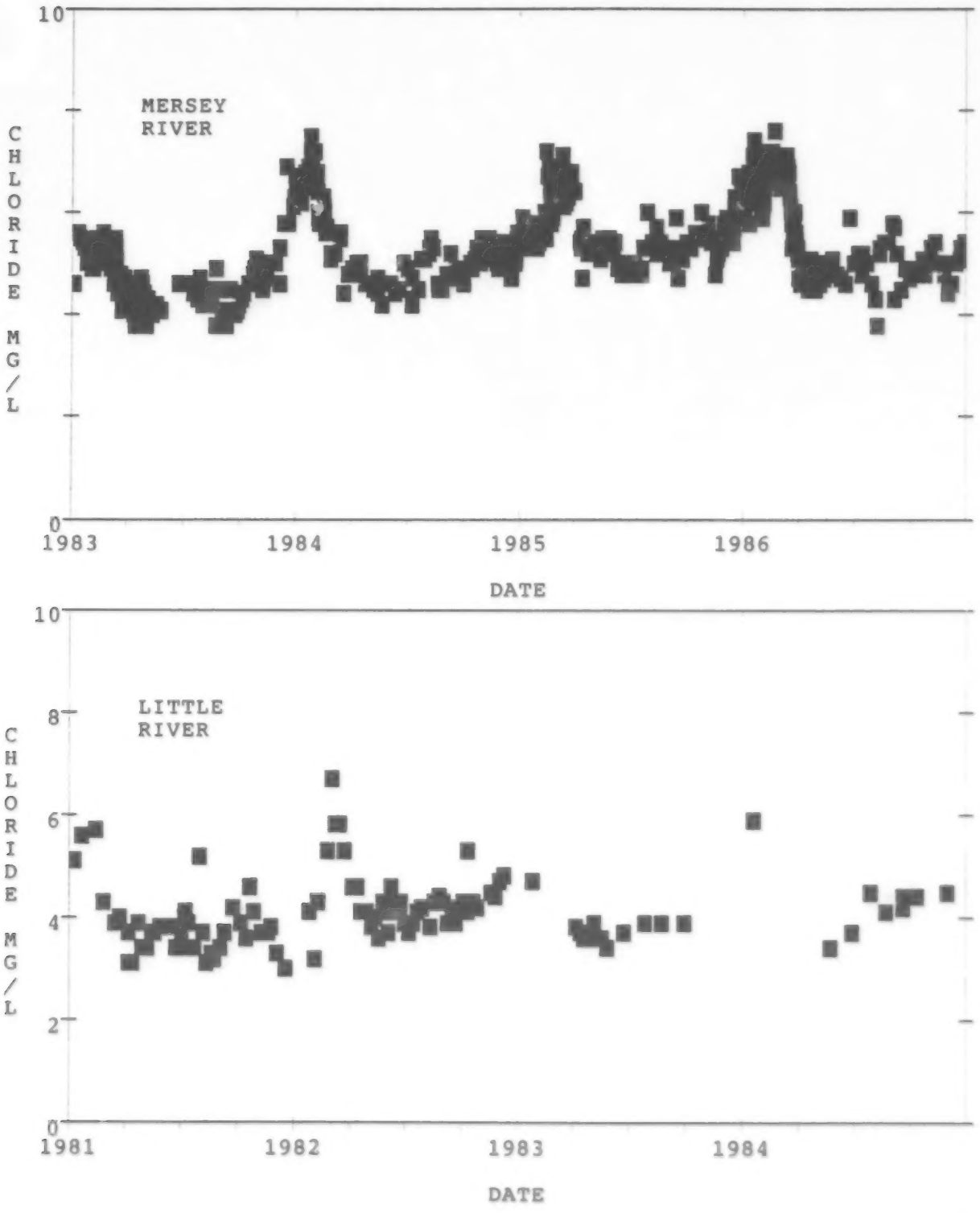

FIGURE 19: CHLORIDE CONCENTRATIONS IN TWO HEADWATER LAKES

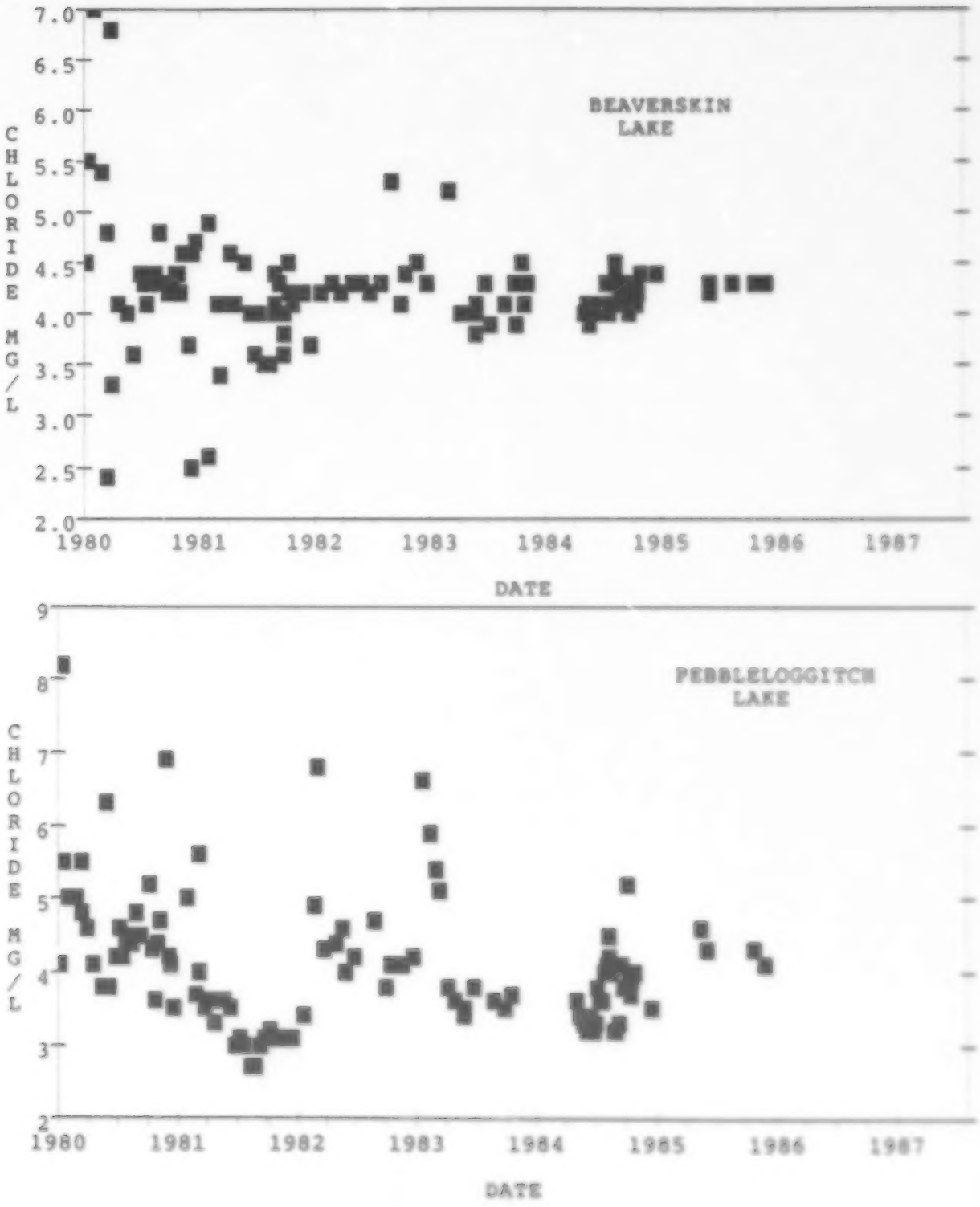

FIGURE 20 :CHLORIDE CONCENTRATIONS IN WATER
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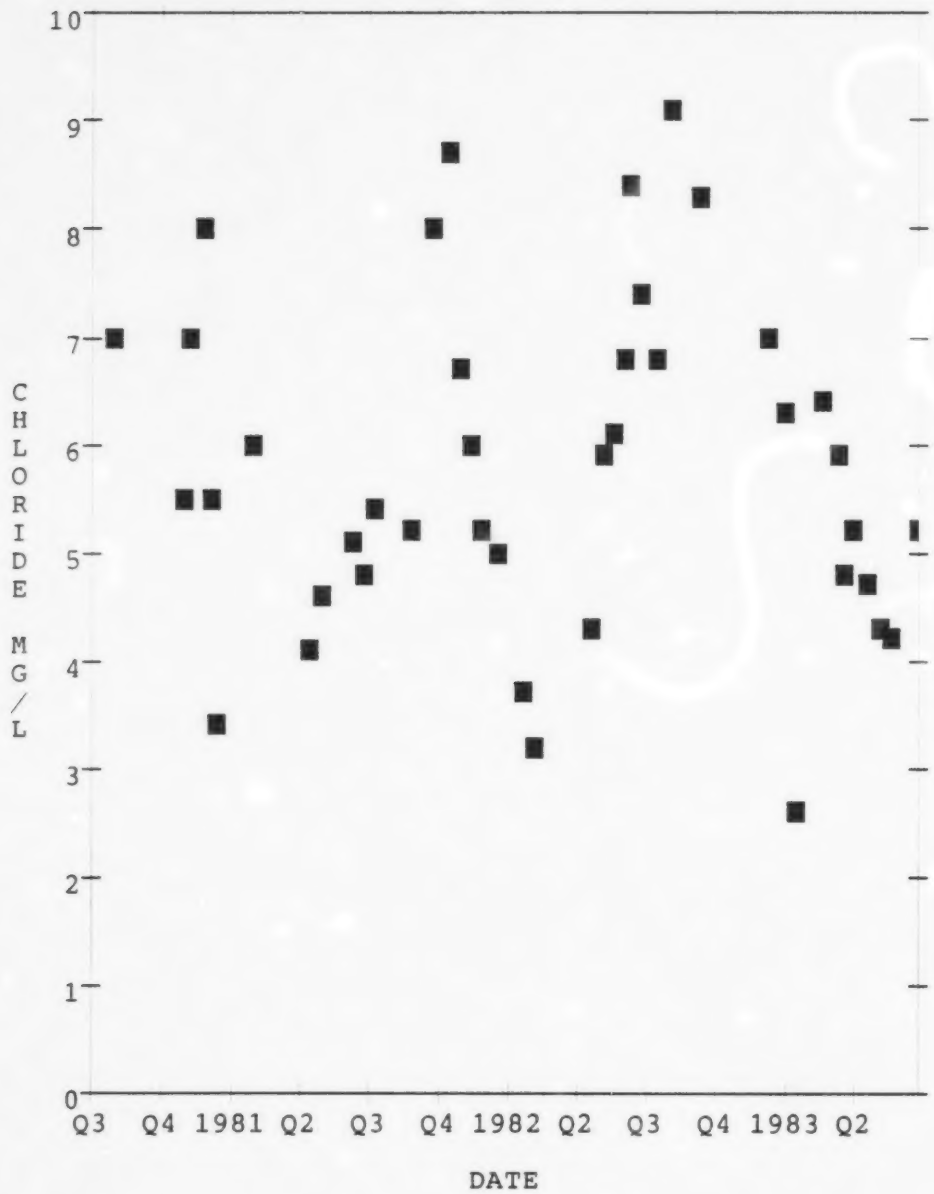

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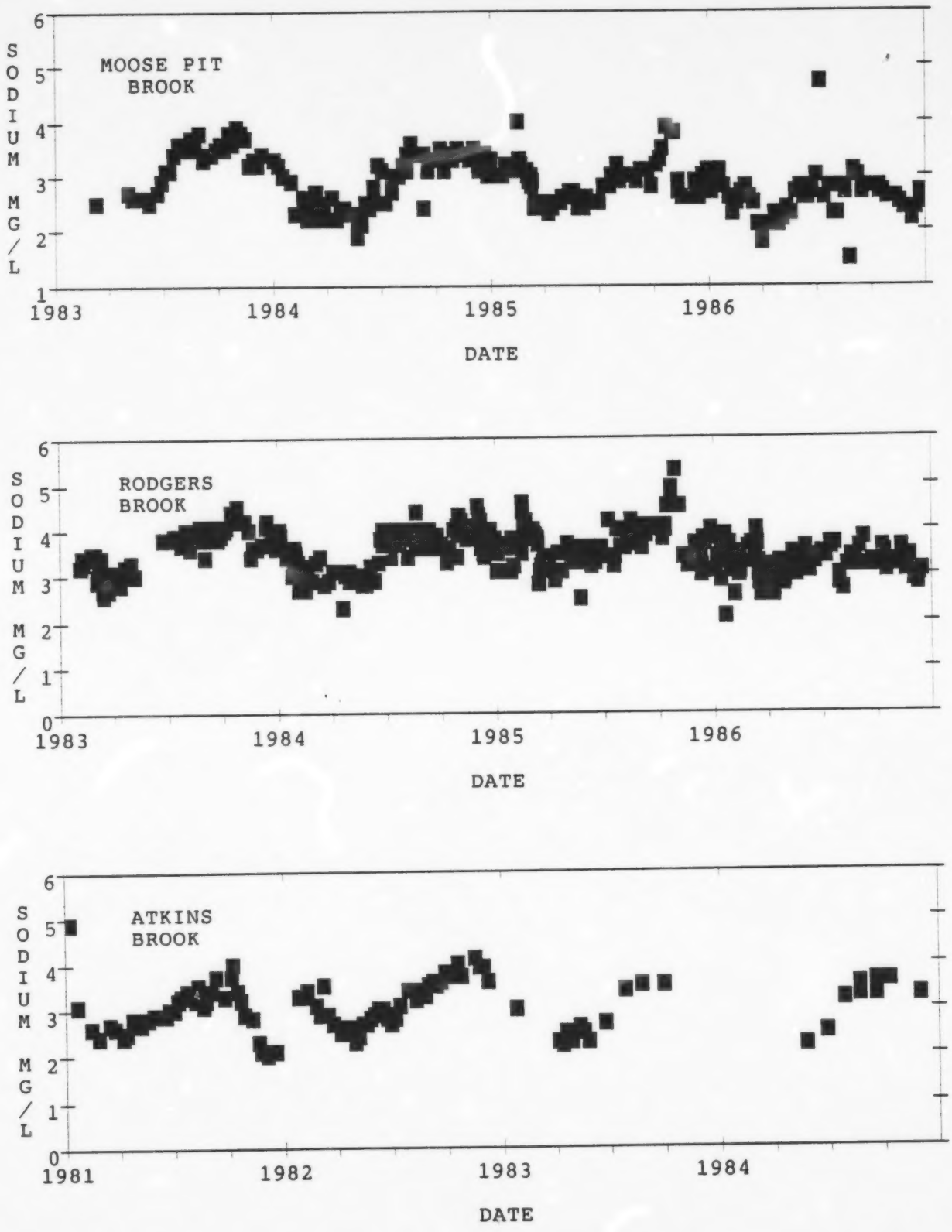

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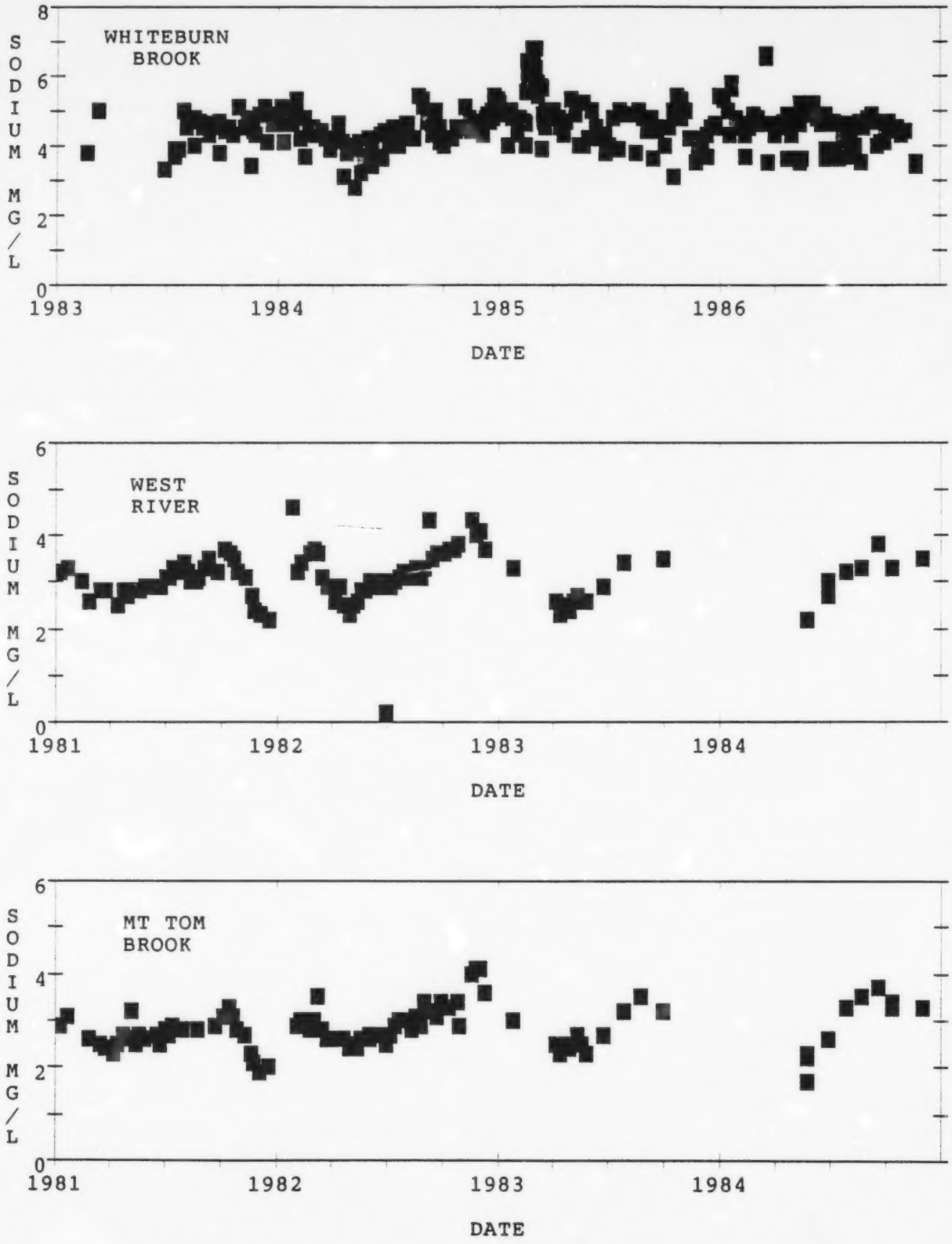


FIGURE 23: SODIUM CONCENTRATIONS IN TWO HIGH ORDER RIVERS

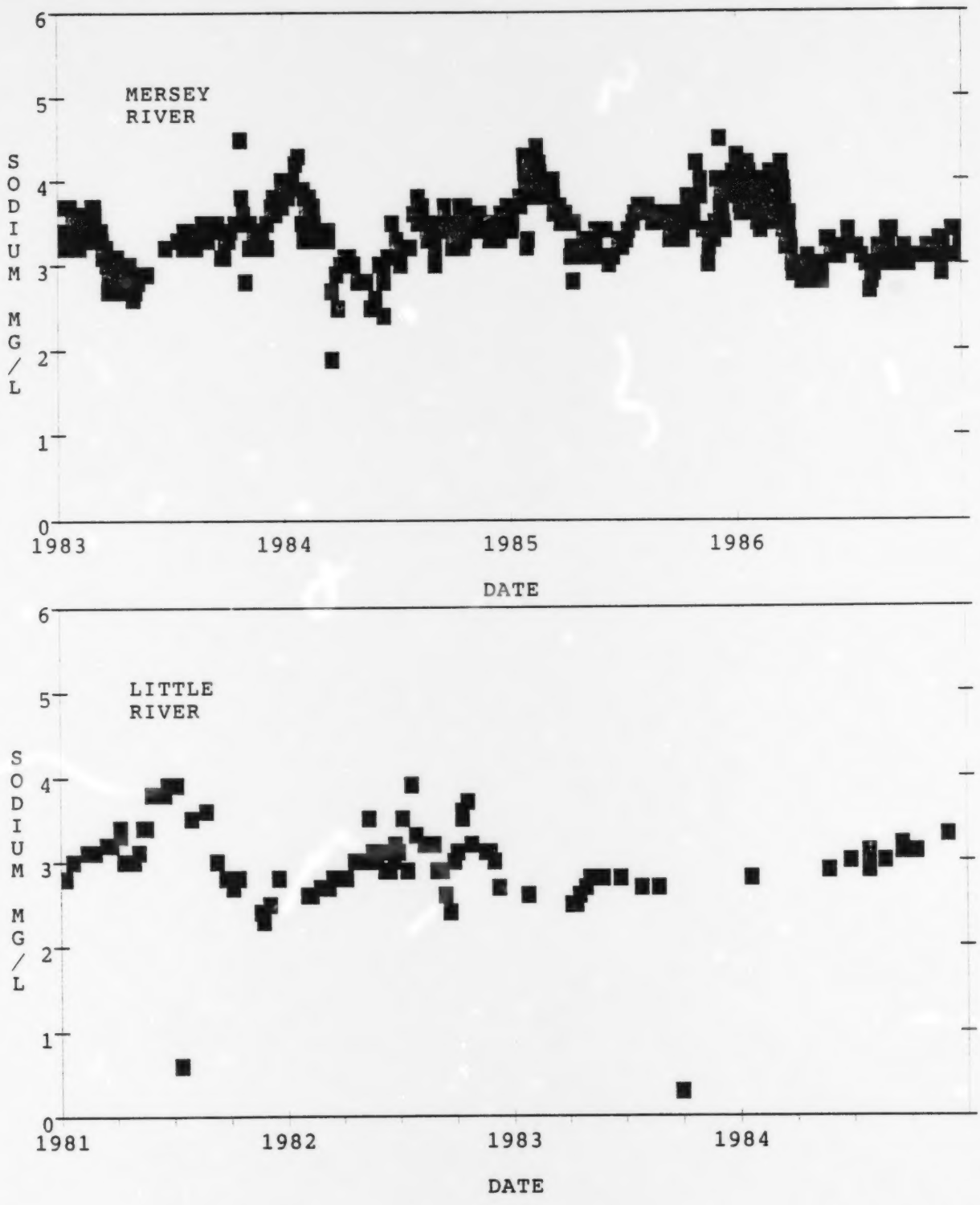


FIGURE 24: SODIUM CONCENTRATIONS IN TWO HEADWATER LAKES

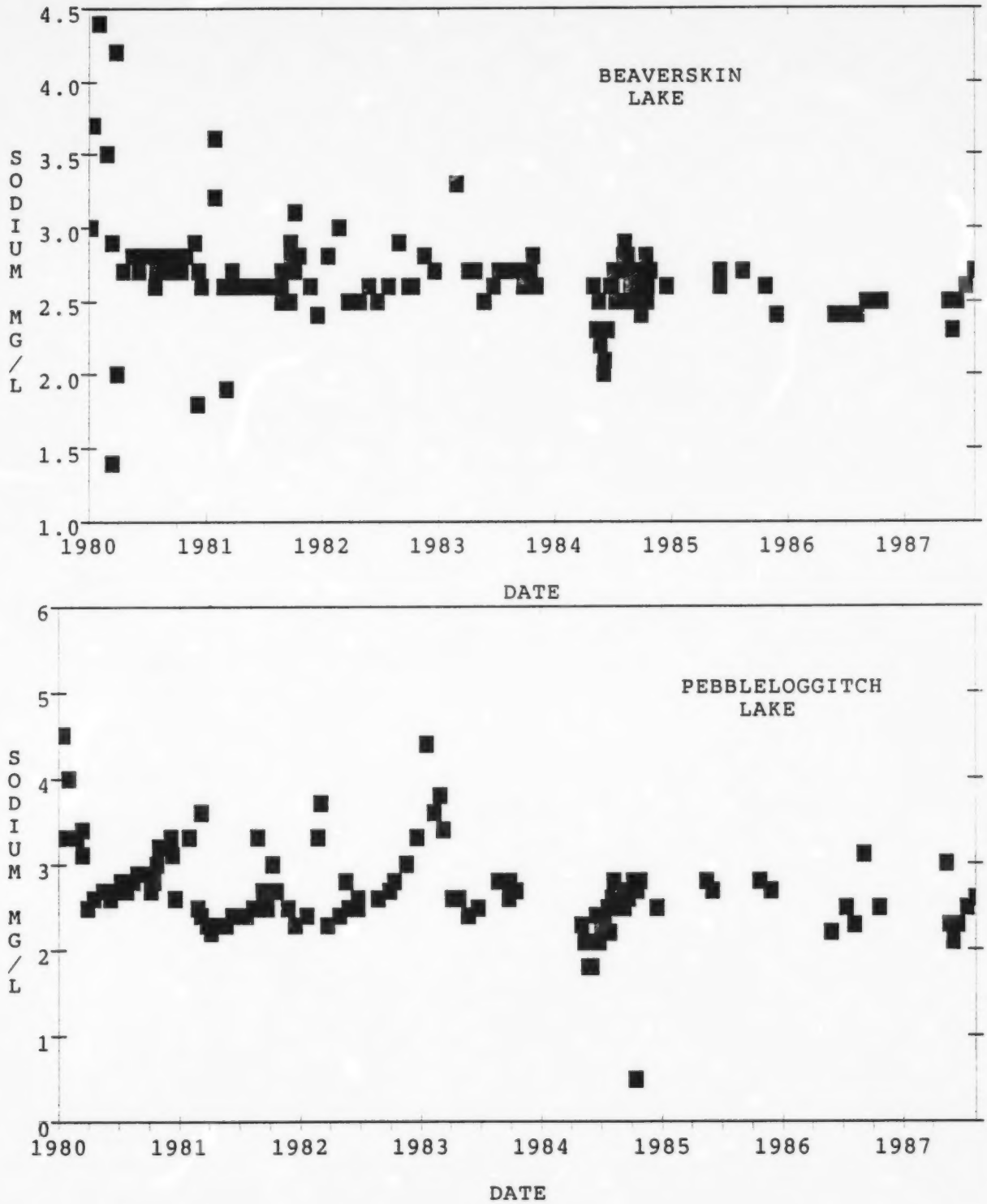


FIGURE 25 : SODIUM CONCENTRATIONS IN WATER FROM PEBBLELOGGITCH WELL

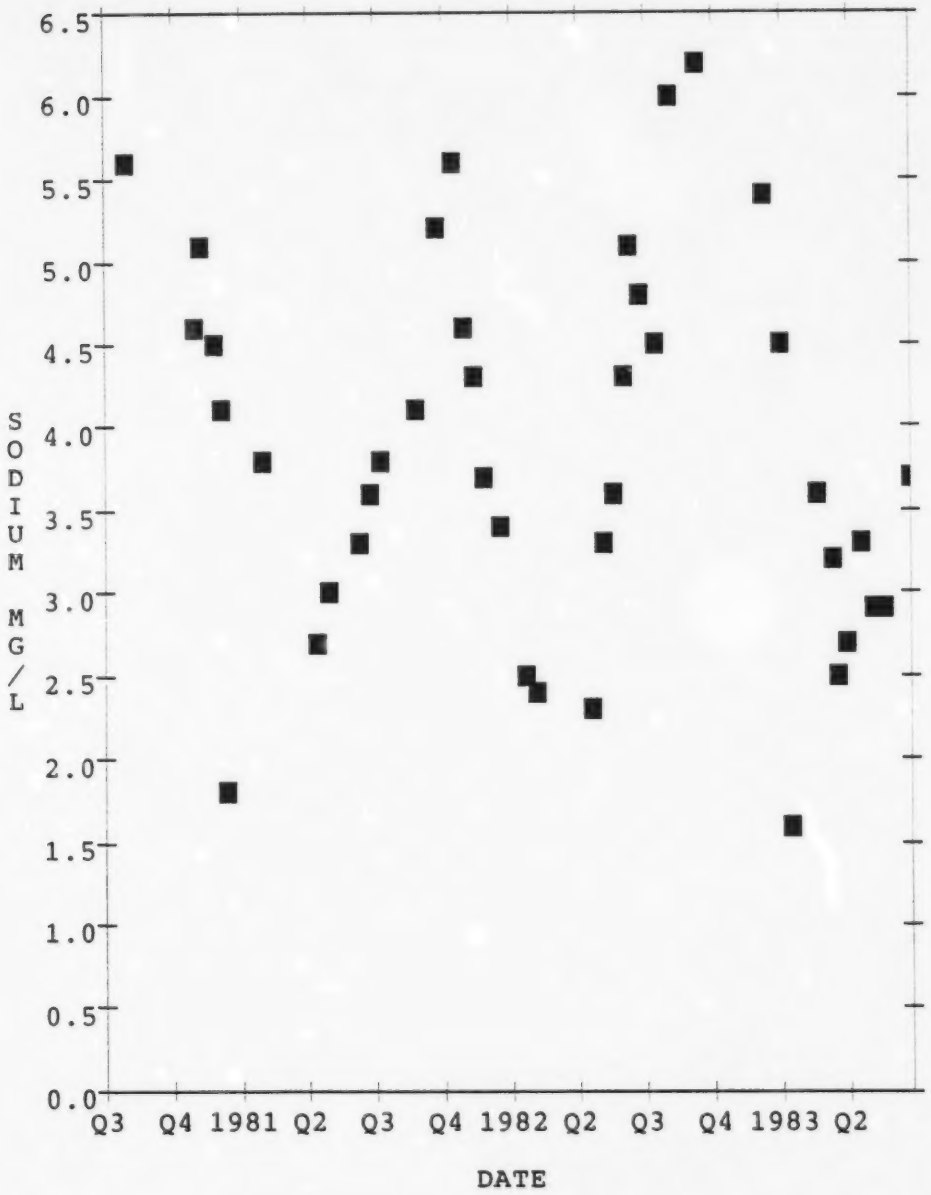


FIGURE 26: THE RATIO OF SODIUM TO CHLORIDE IN THREE FIRST ORDER STREAMS

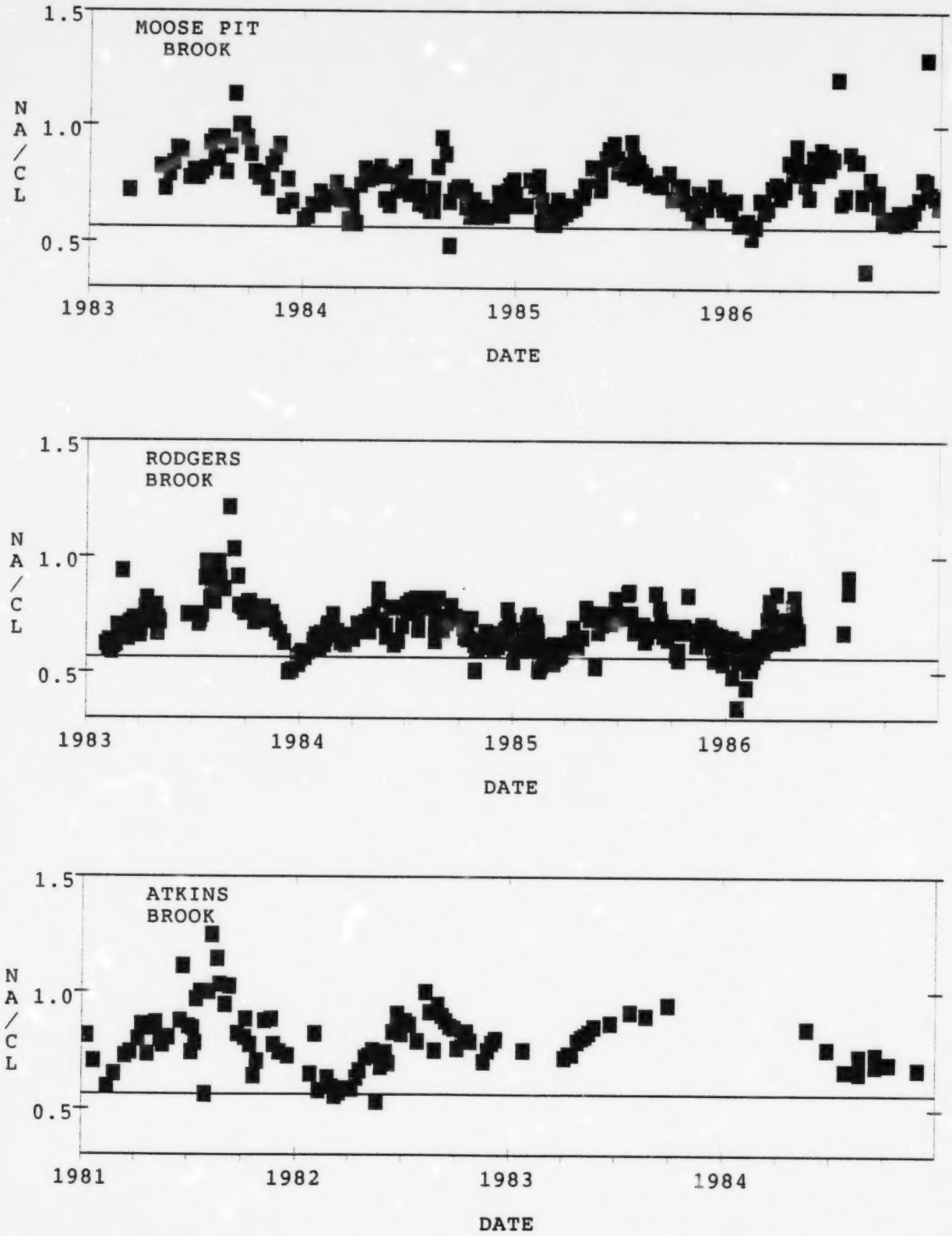


FIGURE 27: THE RATIO OF SODIUM TO CHLORIDE IN THREE STREAMS WHICH DRAIN HEADWATER LAKES

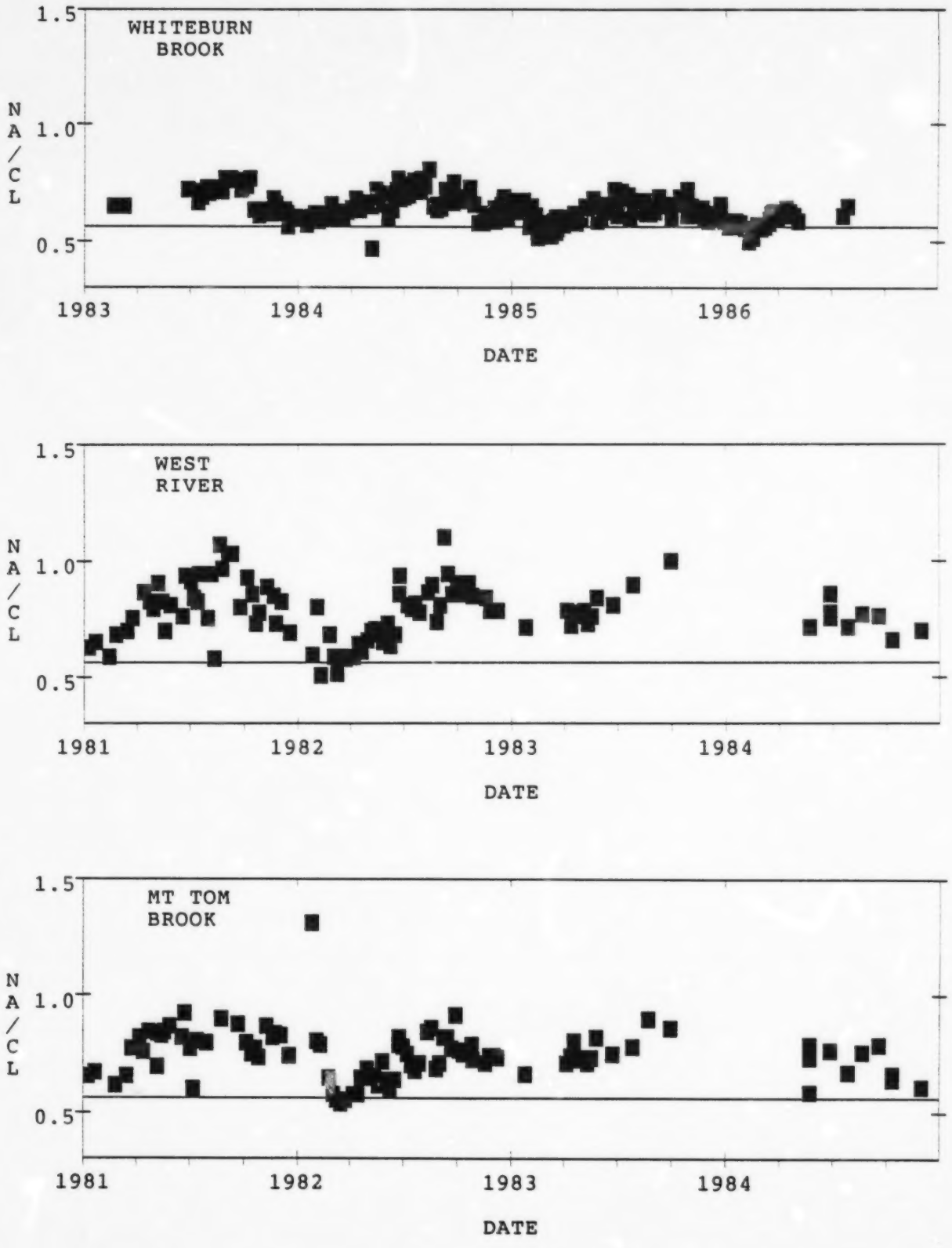


FIGURE 28: THE RATIO OF SODIUM TO CHLORIDE IN TWO HIGH ORDER RIVERS

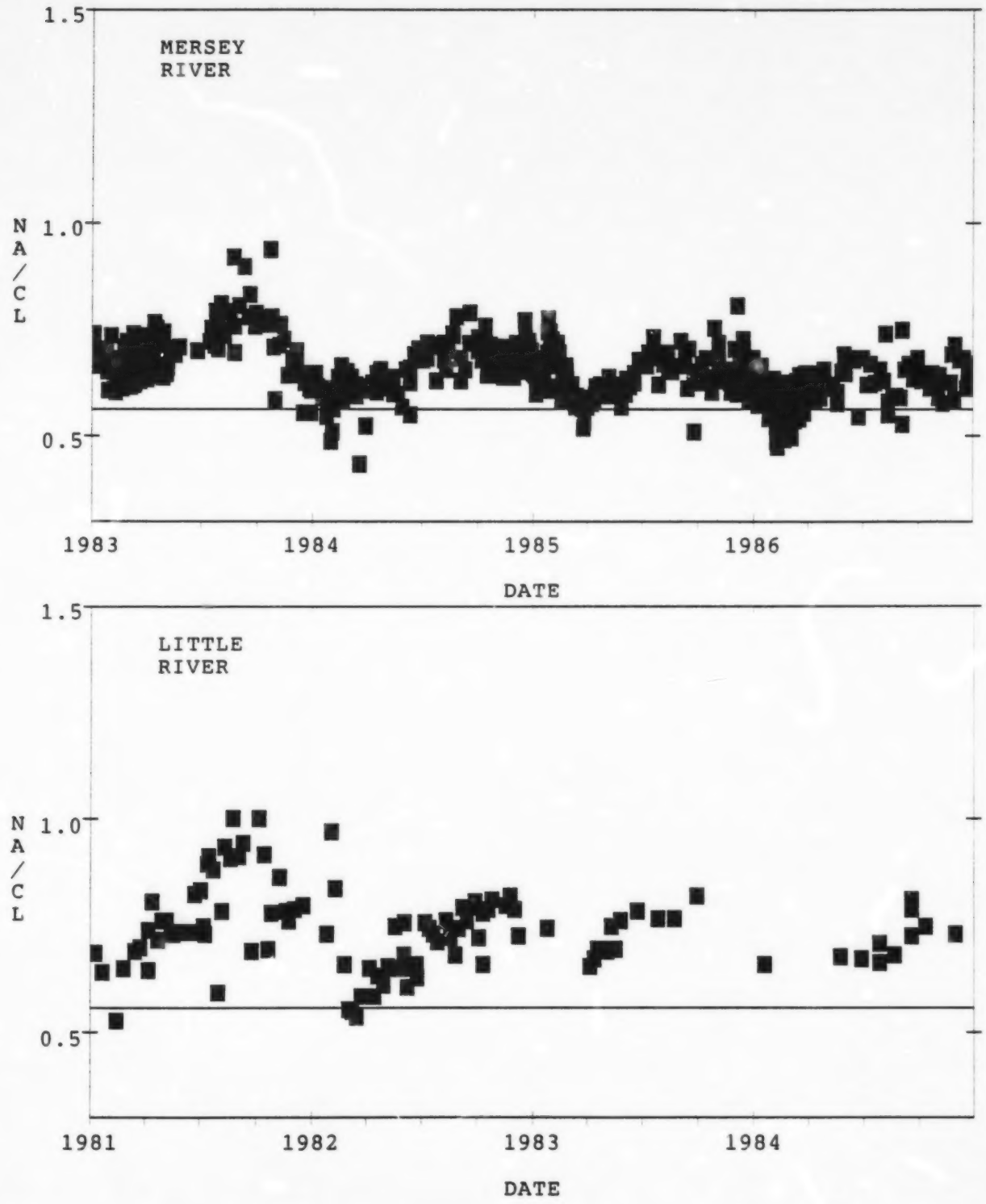


FIGURE 29: THE RATIO OF SODIUM TO CHLORIDE IN TWO HEADWATER LAKES

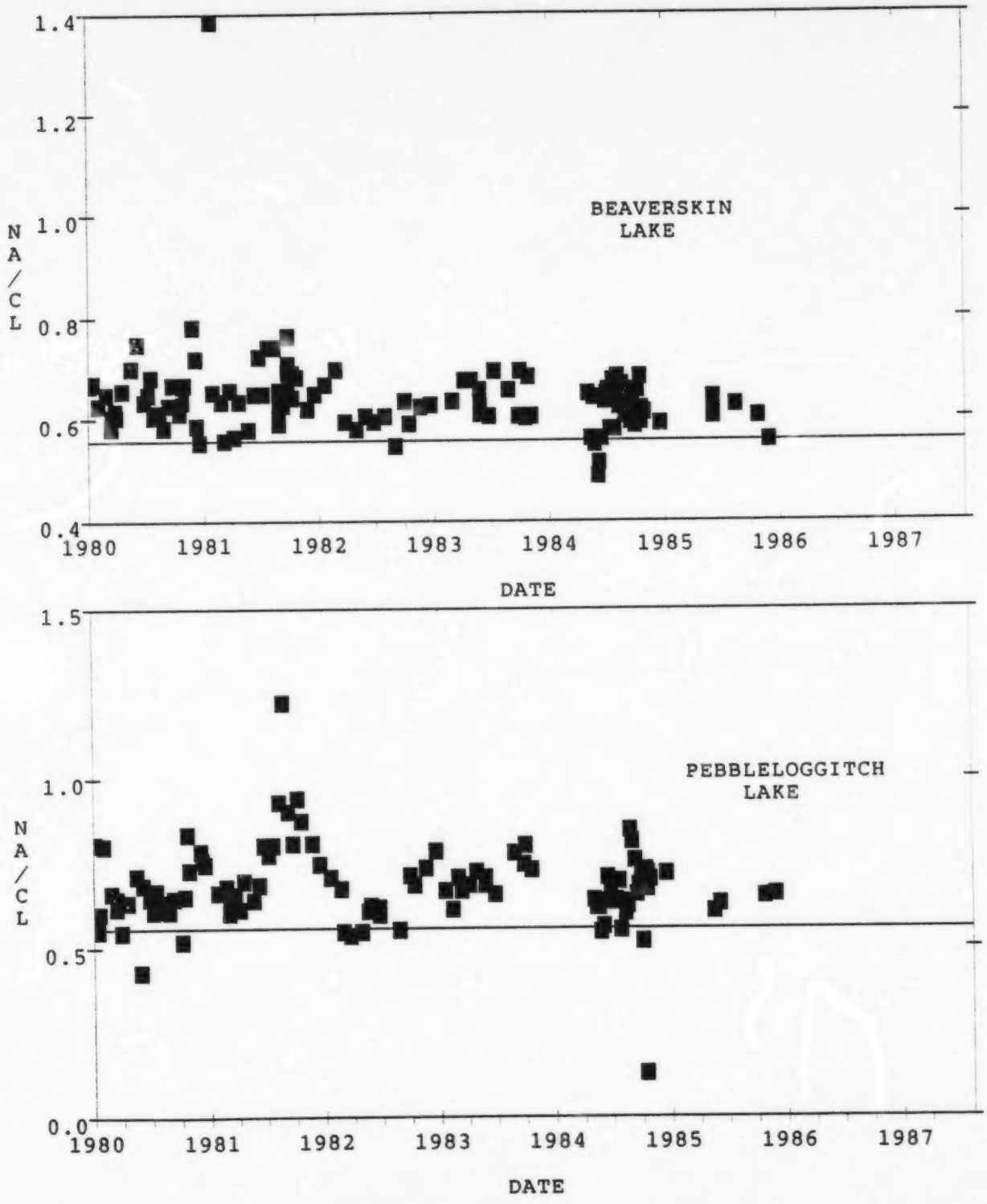


FIGURE 30: THE RELATIONSHIP OF SODIUM AND CHLORIDE IN WET PRECIPITATION COLLECTED AT KEJIMKUJIK NATIONAL PARK

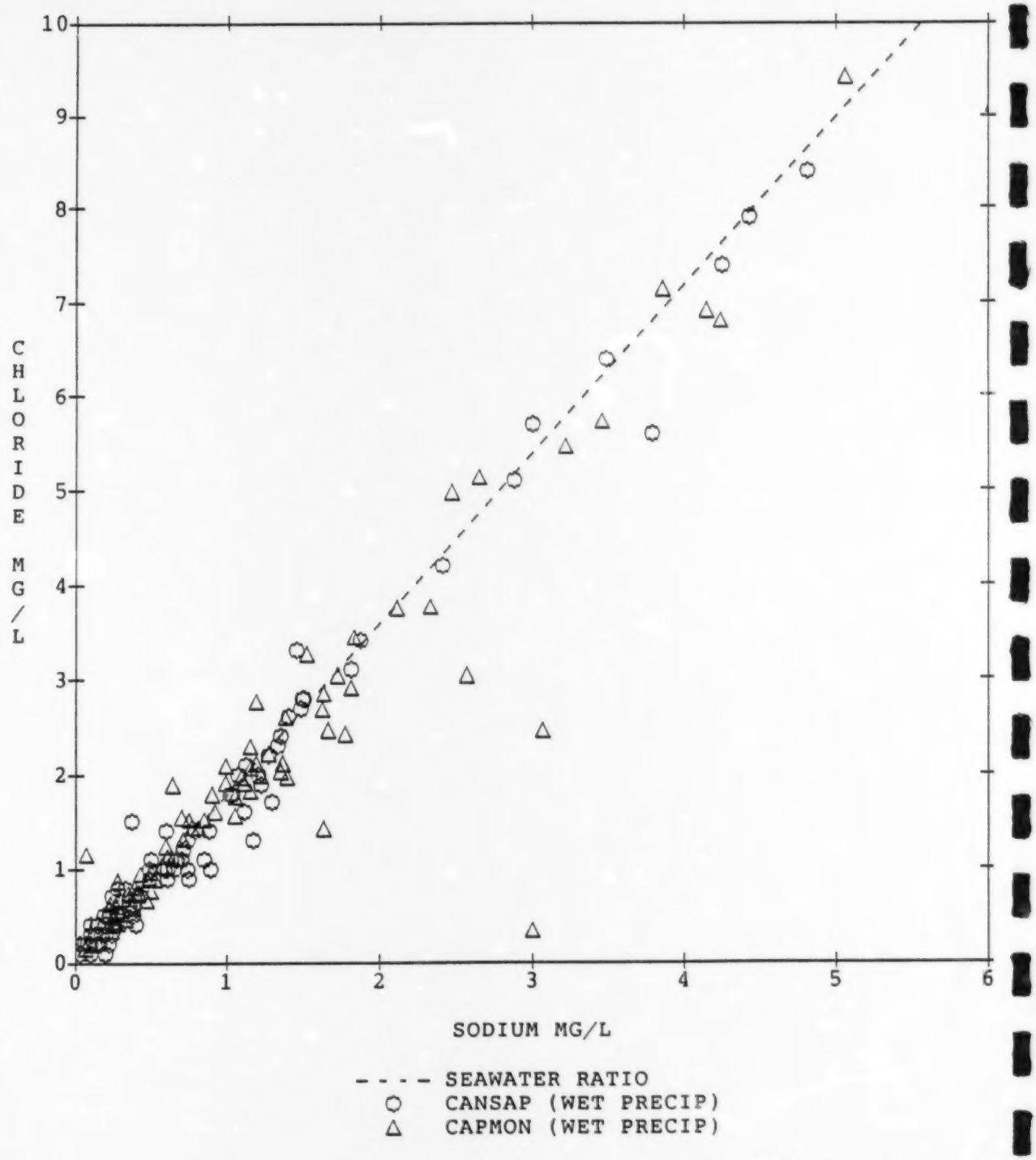


FIGURE 31: THE RELATIONSHIP OF SODIUM TO CHLORIDE IN AIR, BULK PRECIPITATION AND THROUGHFALL PRECIPITATION COLLECTED AT KEJIMKUJIK NATIONAL PARK

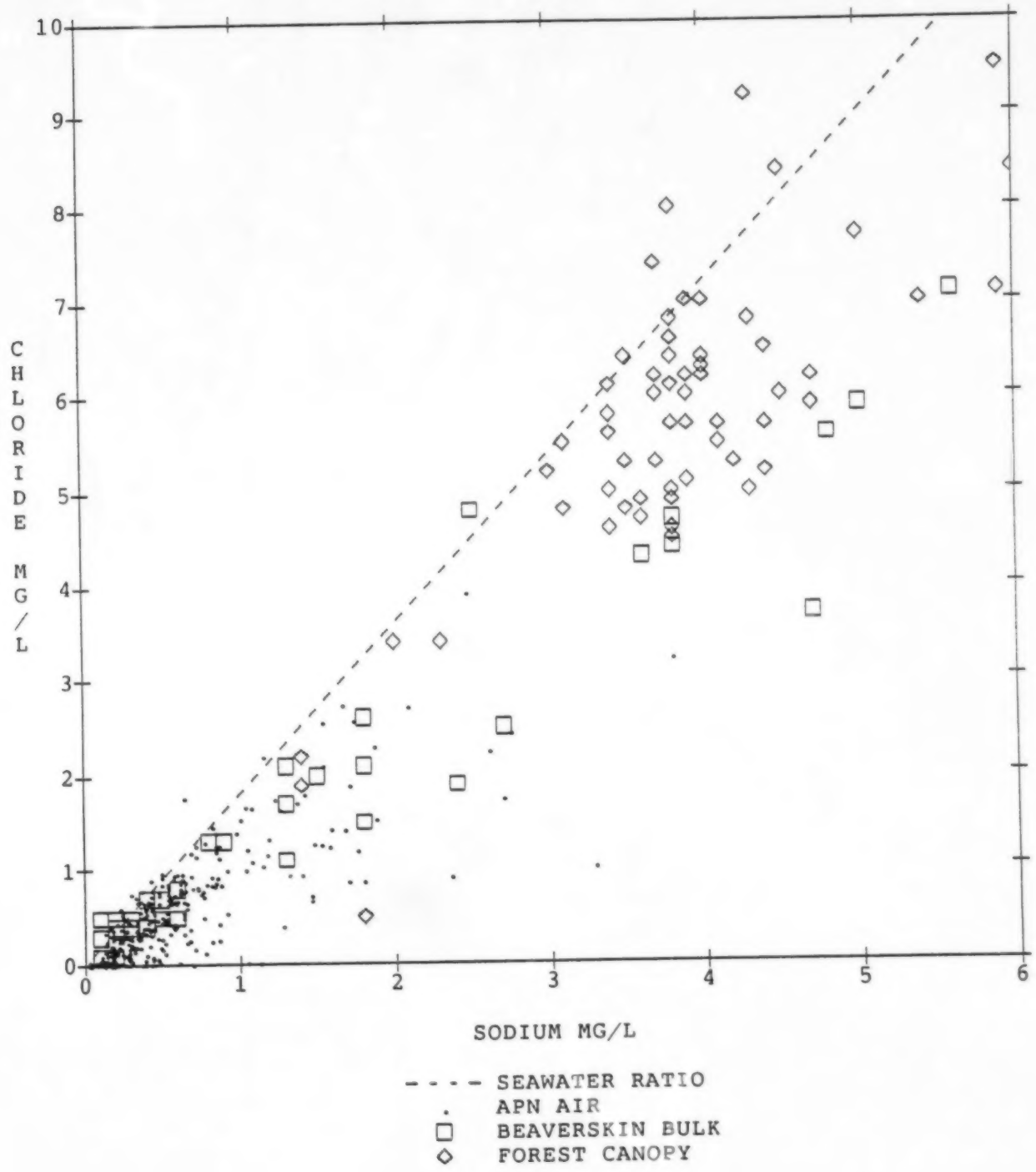


FIGURE 32 :CALCIUM CONCENTRATIONS IN WATER
FROM PEBBLELOGGITCH WELL

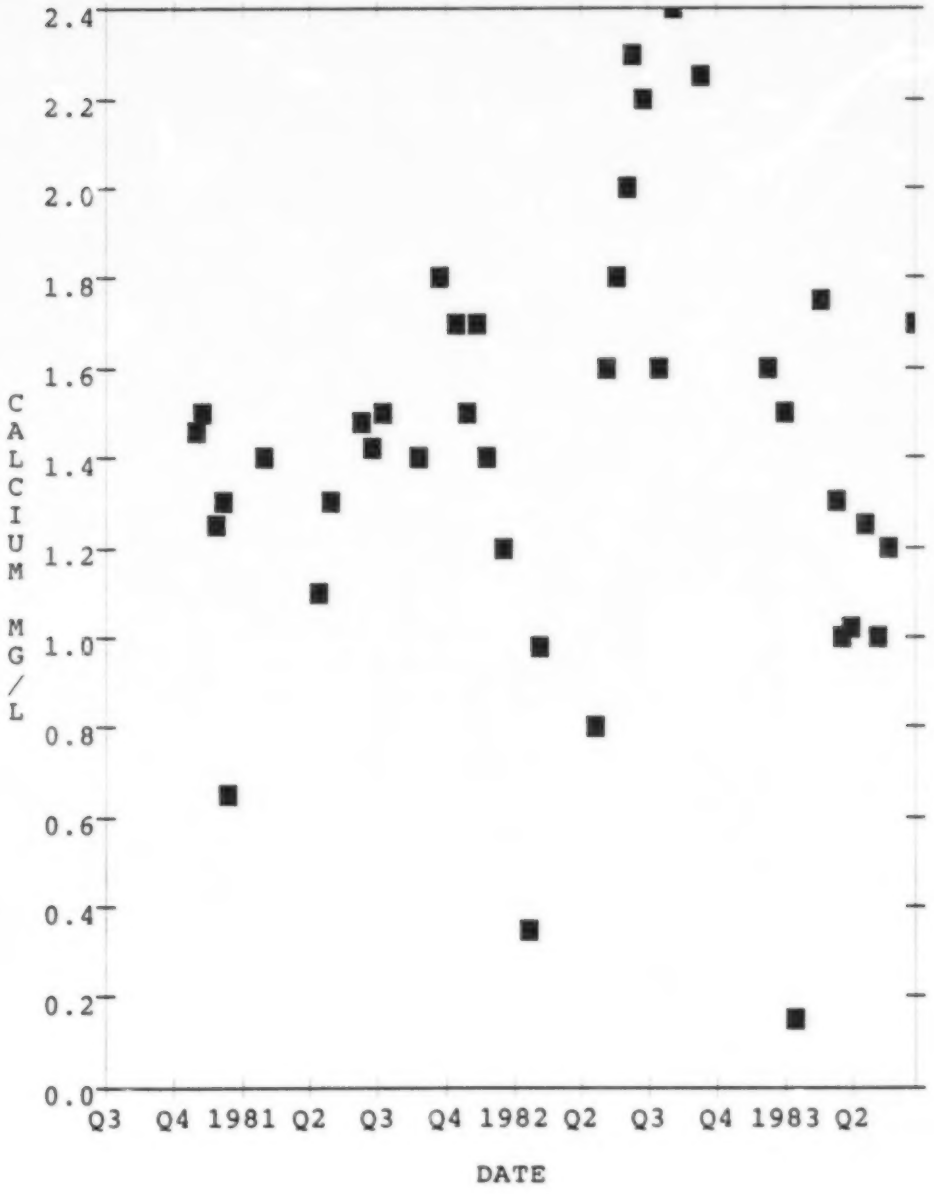


FIGURE 33: CALCIUM CONCENTRATIONS IN THREE FIRST ORDER STREAMS

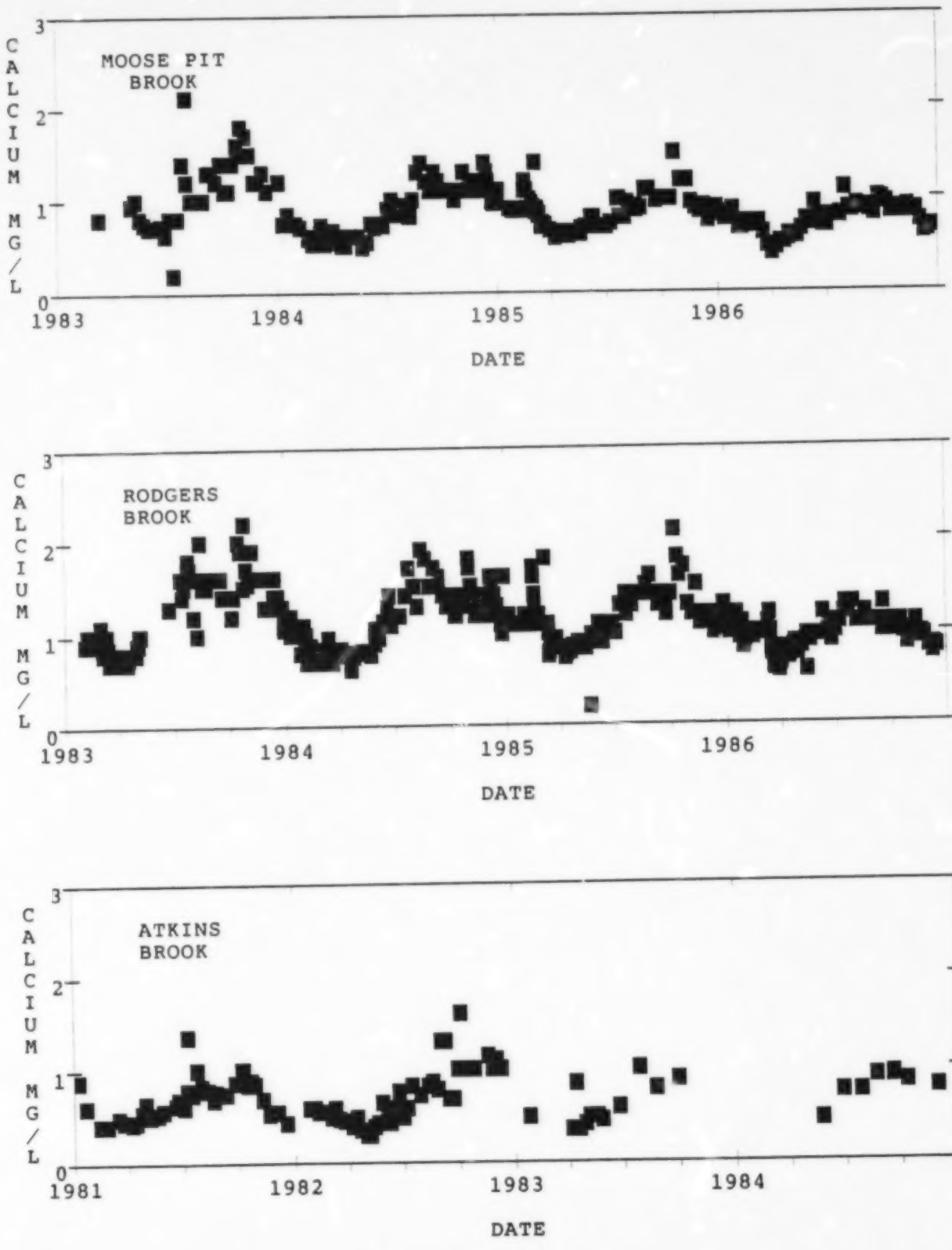


FIGURE 34: CALCIUM CONCENTRATIONS IN THREE STREAMS WHICH DRAIN HEADWATER LAKES

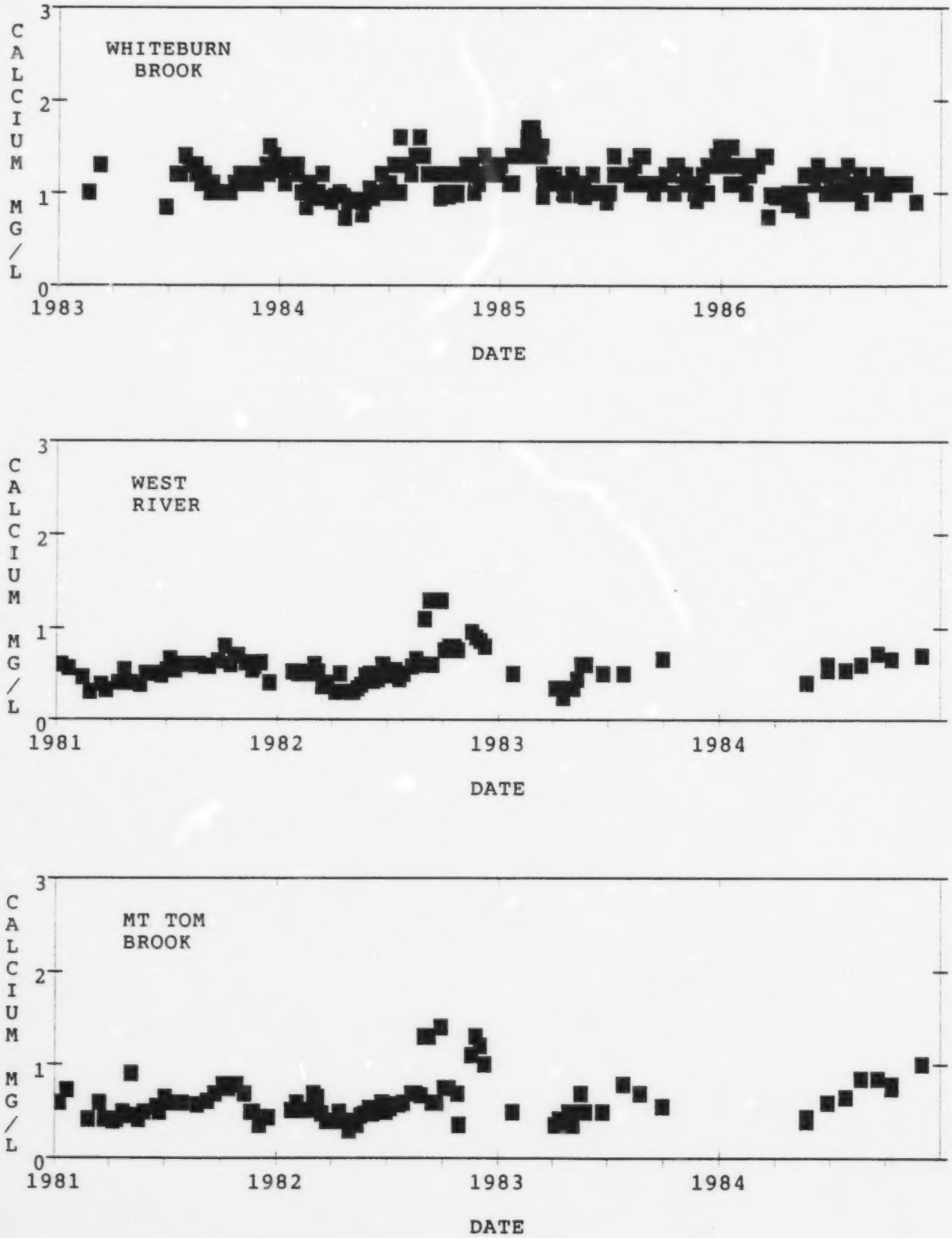


FIGURE 35: CALCIUM CONCENTRATIONS IN TWO HIGH ORDER RIVERS

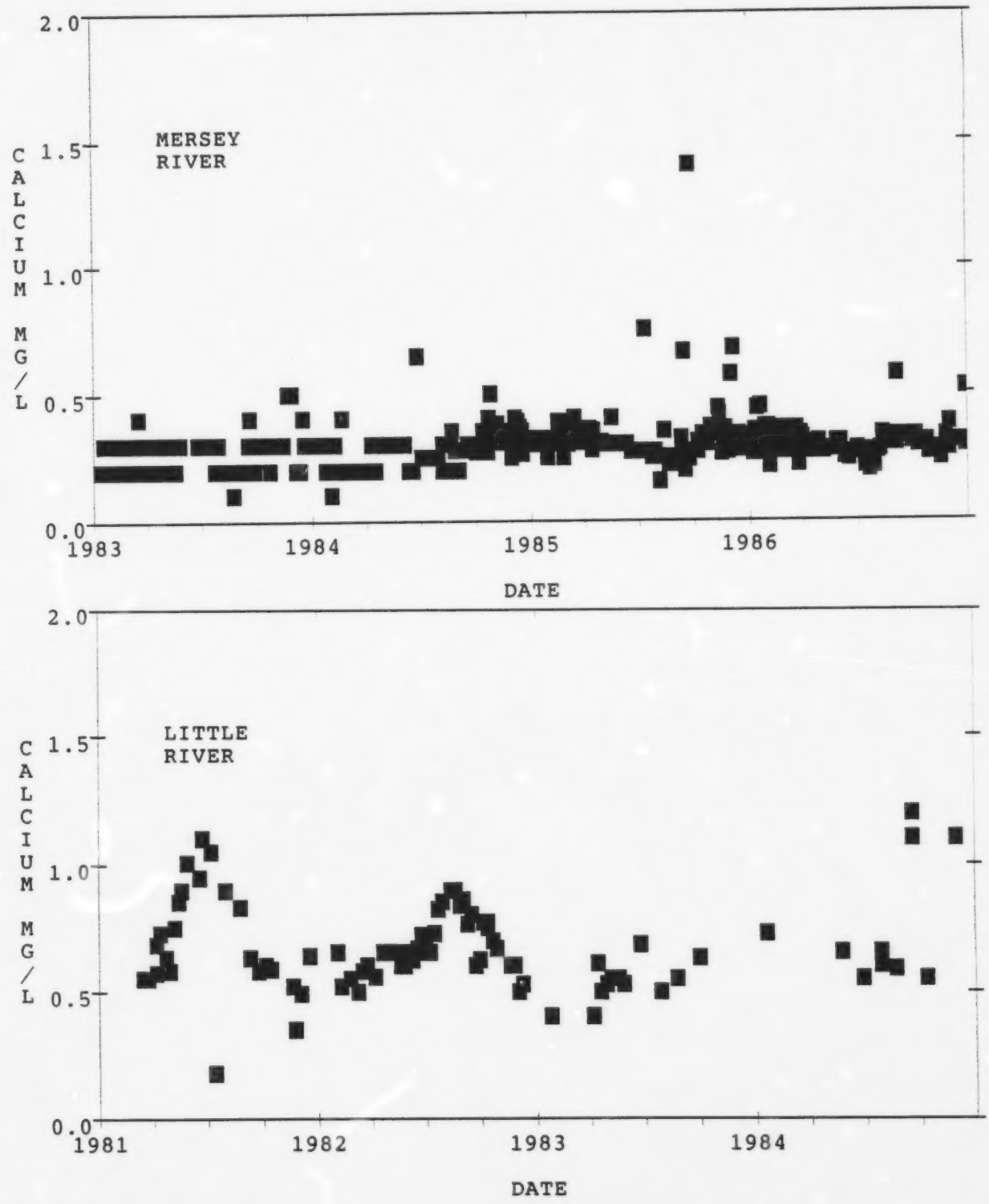


FIGURE 36: CALCIUM CONCENTRATIONS IN TWO HEADWATER LAKES

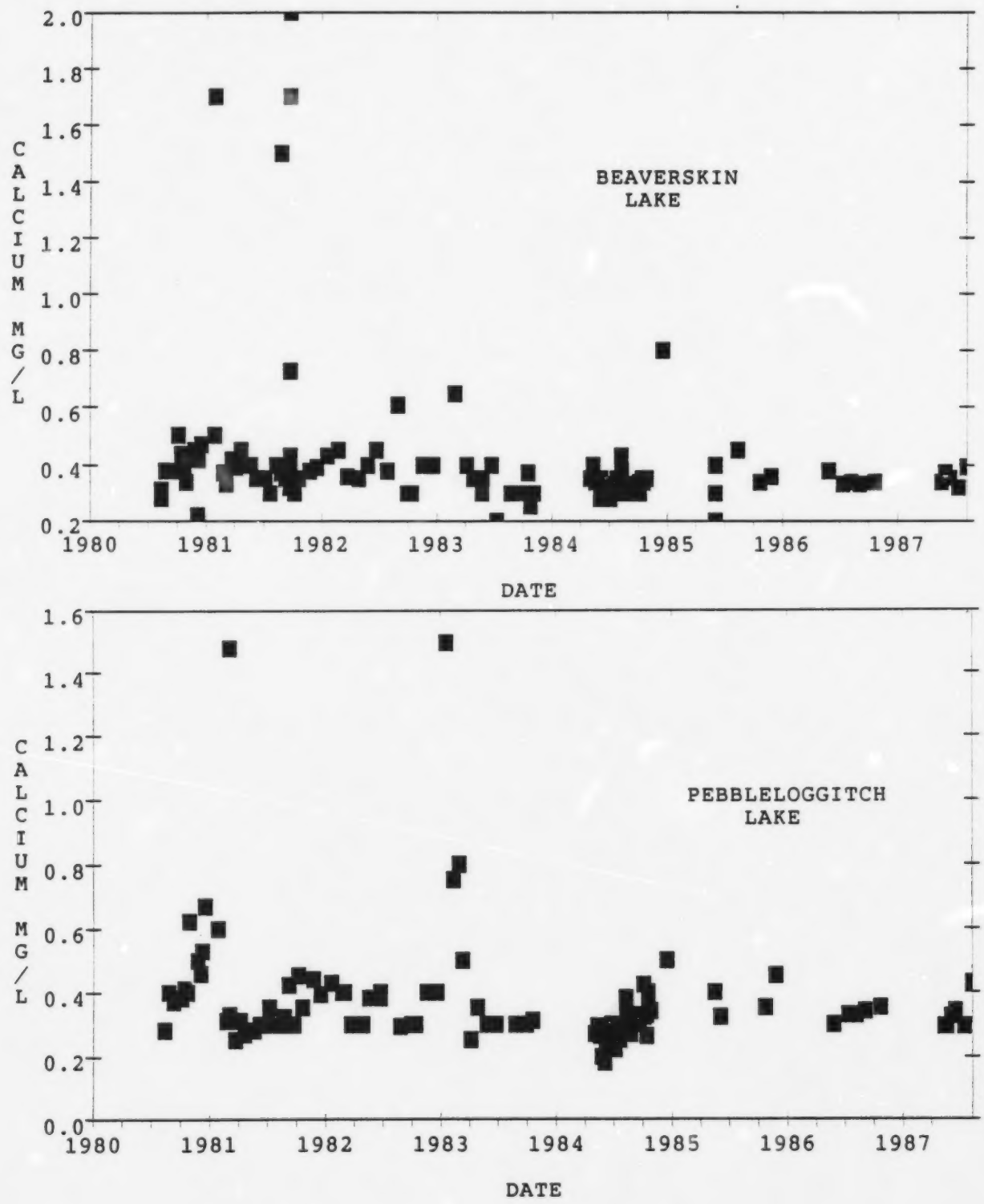


FIGURE 37: MAGNESIUM CONCENTRATIONS IN WATER FROM PEBBLELOGGITCH WELL

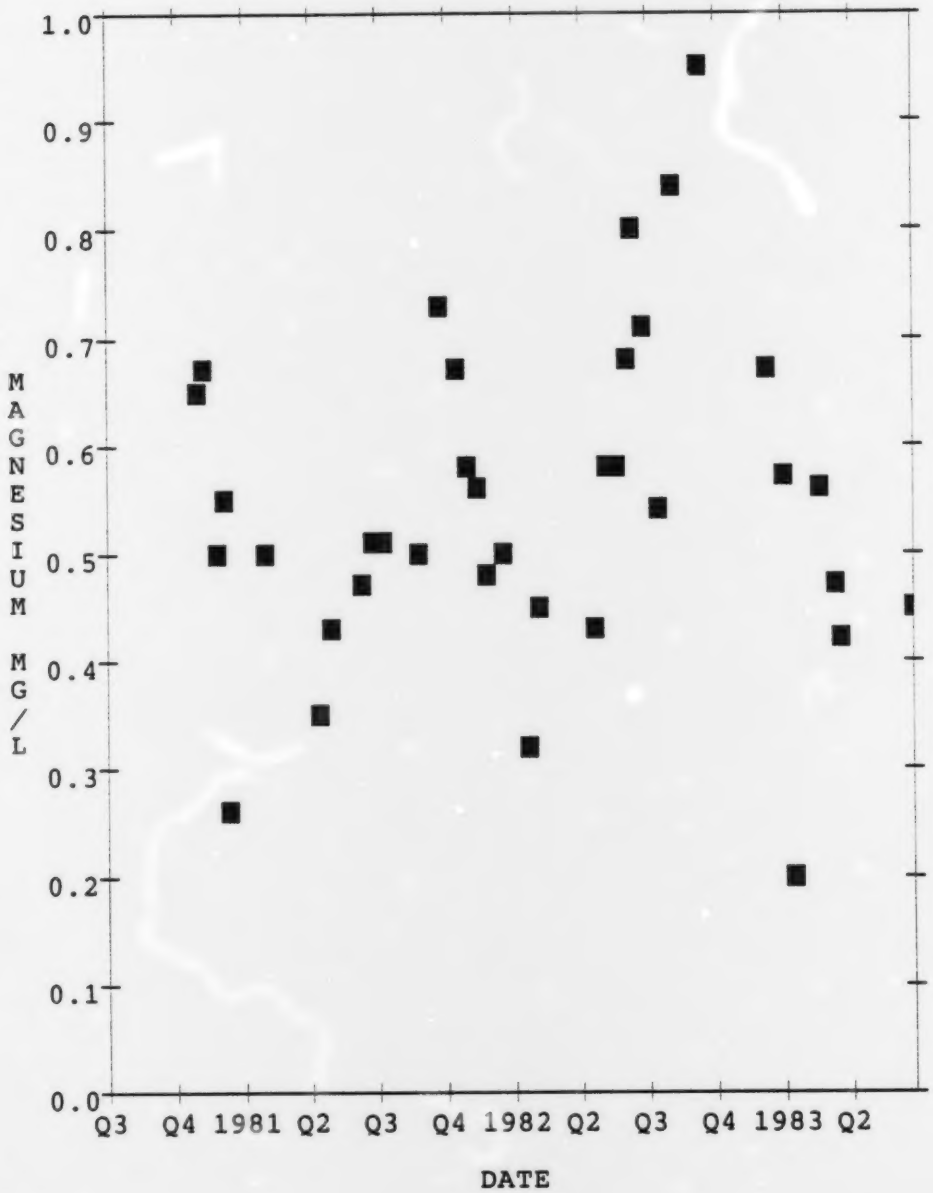


FIGURE 38: MAGNESIUM CONCENTRATIONS IN THREE FIRST ORDER STREAMS

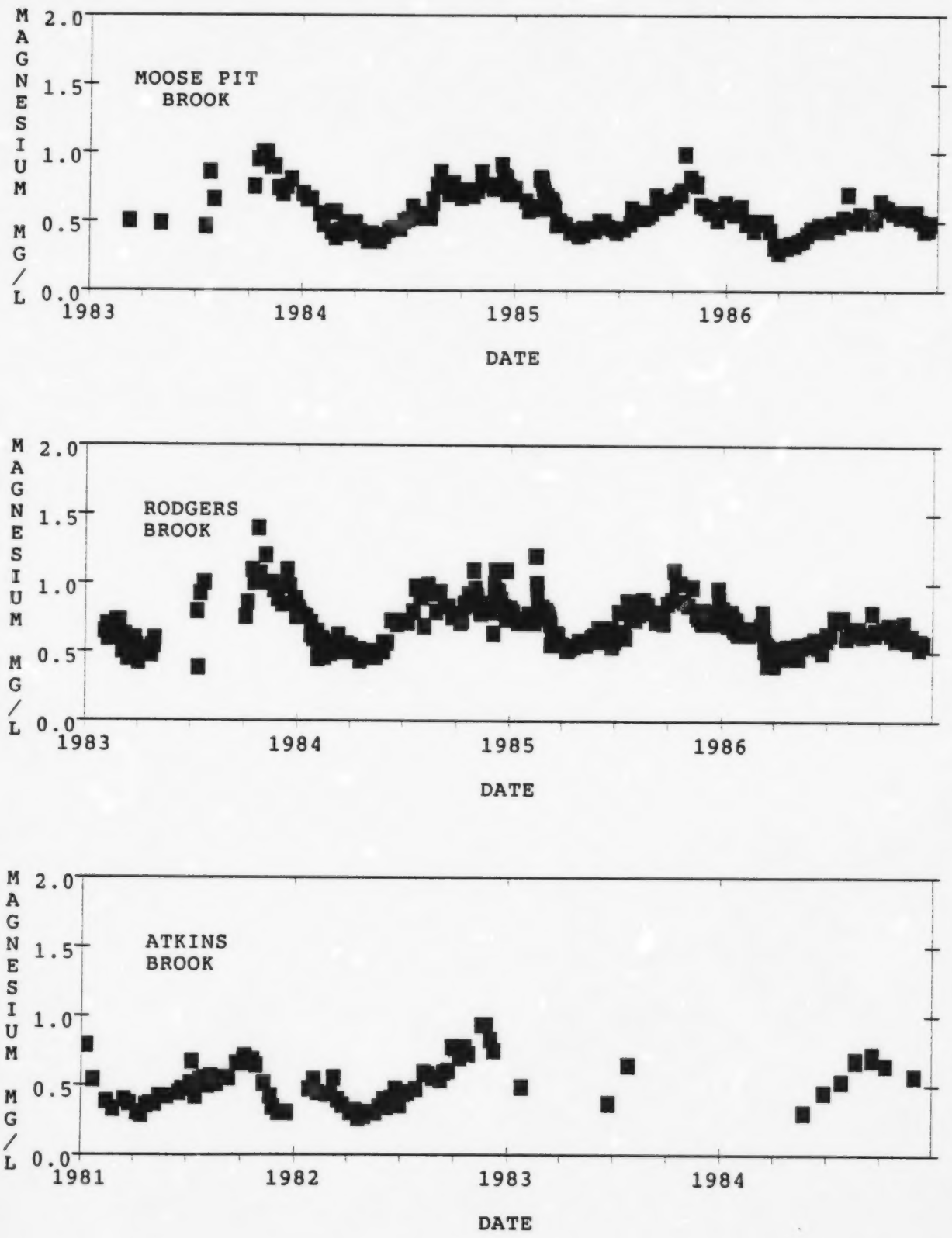


FIGURE 39: MAGNESIUM CONCENTRATIONS IN THREE STREAMS WHICH DRAIN HEADWATER LAKES

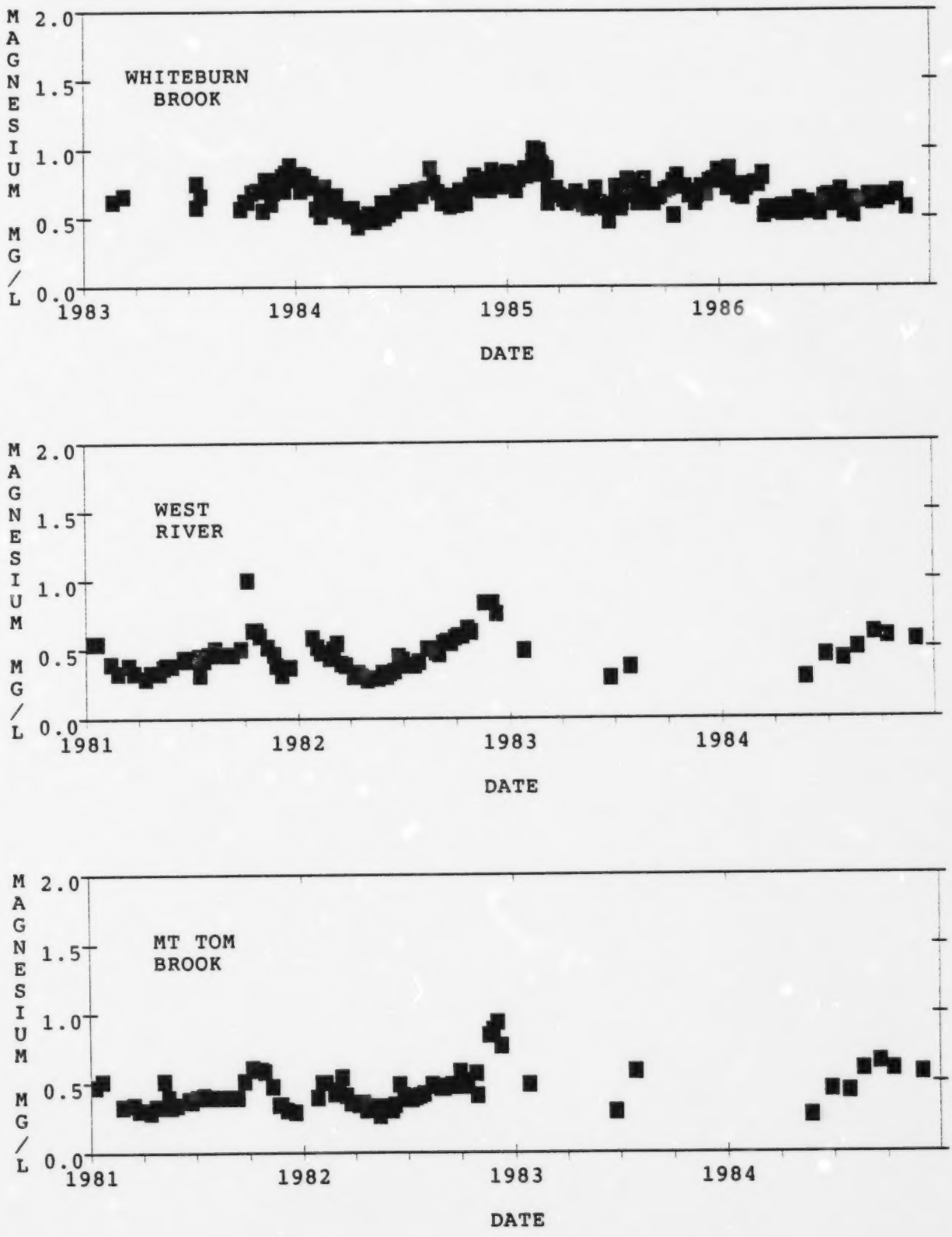


FIGURE 40: MAGNESIUM CONCENTRATIONS IN TWO HIGH ORDER RIVERS

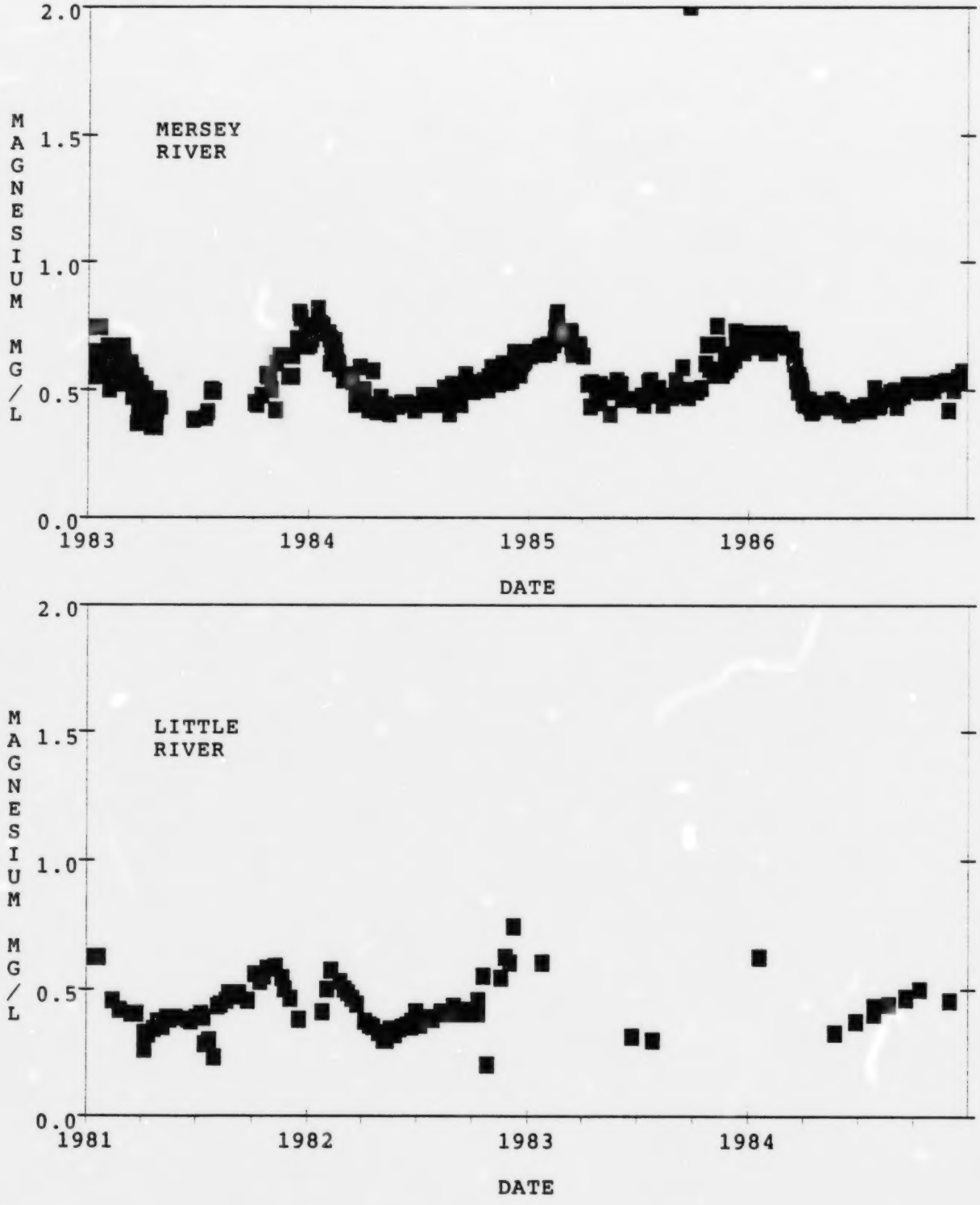


FIGURE 41: MAGNESIUM CONCENTRATIONS IN TWO HEADWATER LAKES

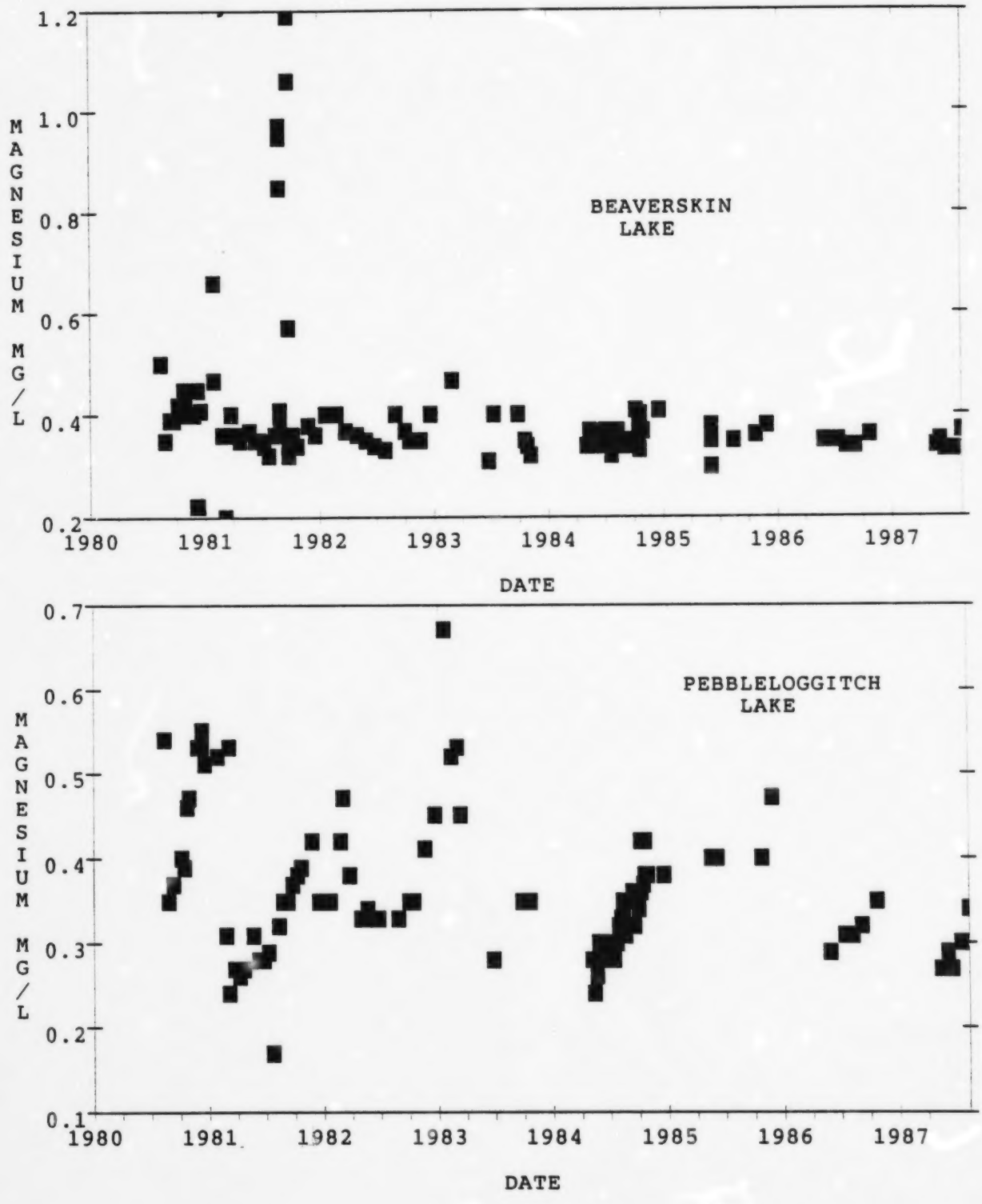


FIGURE 42: WET DEPOSITION AND EXPORT OF SULPHATE FOR THE MERSEY RIVER

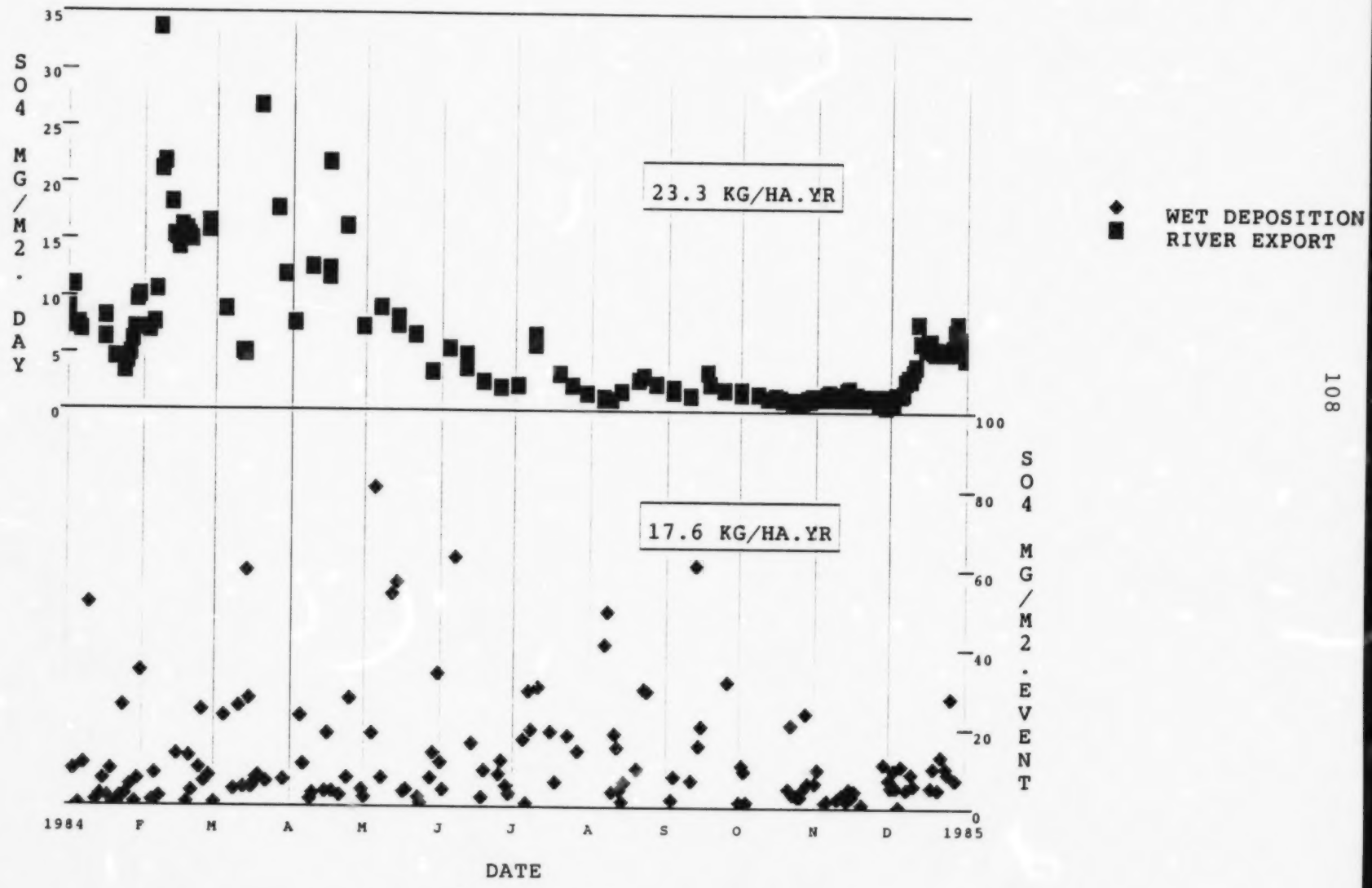


FIGURE 43: WET DEPOSITION AND EXPORT OF SULPHATE FOR MOOSE PIT BROOK

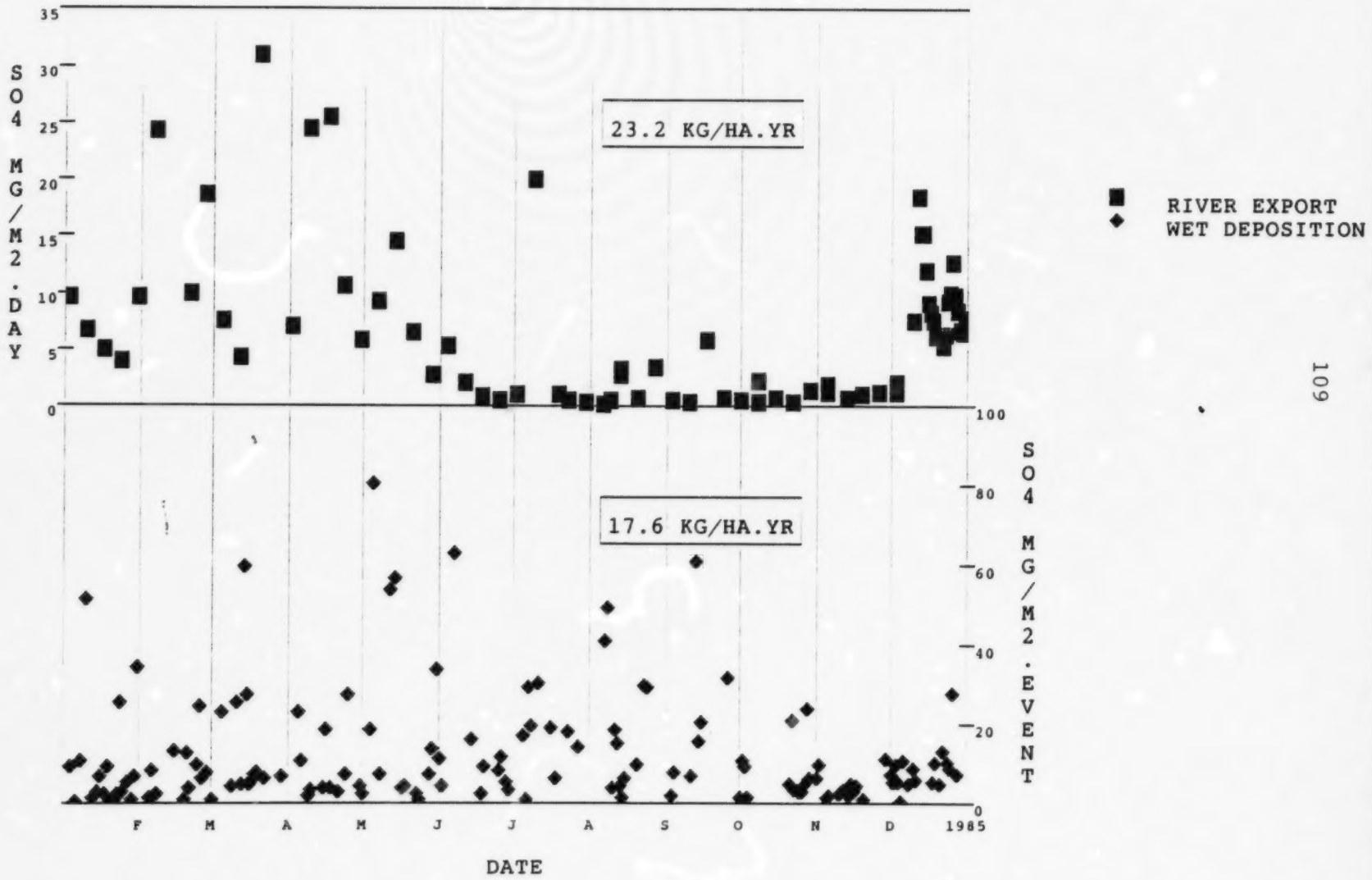


FIGURE 44: SULPHATE CONCENTRATIONS IN THREE FIRST ORDER STREAMS

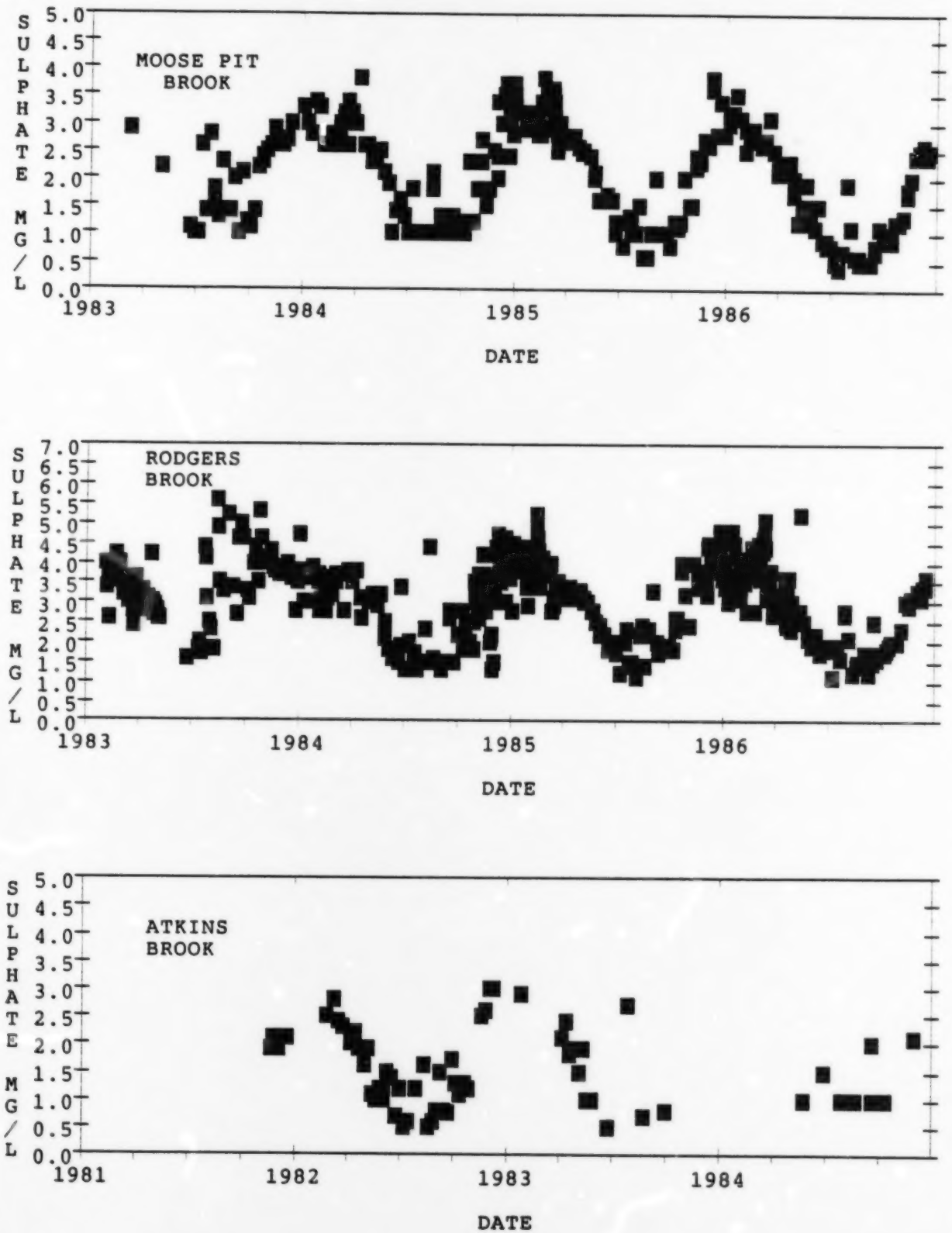


FIGURE 45: SULPHATE CONCENTRATIONS IN THREE STREAMS WHICH DRAIN HEADWATER LAKES

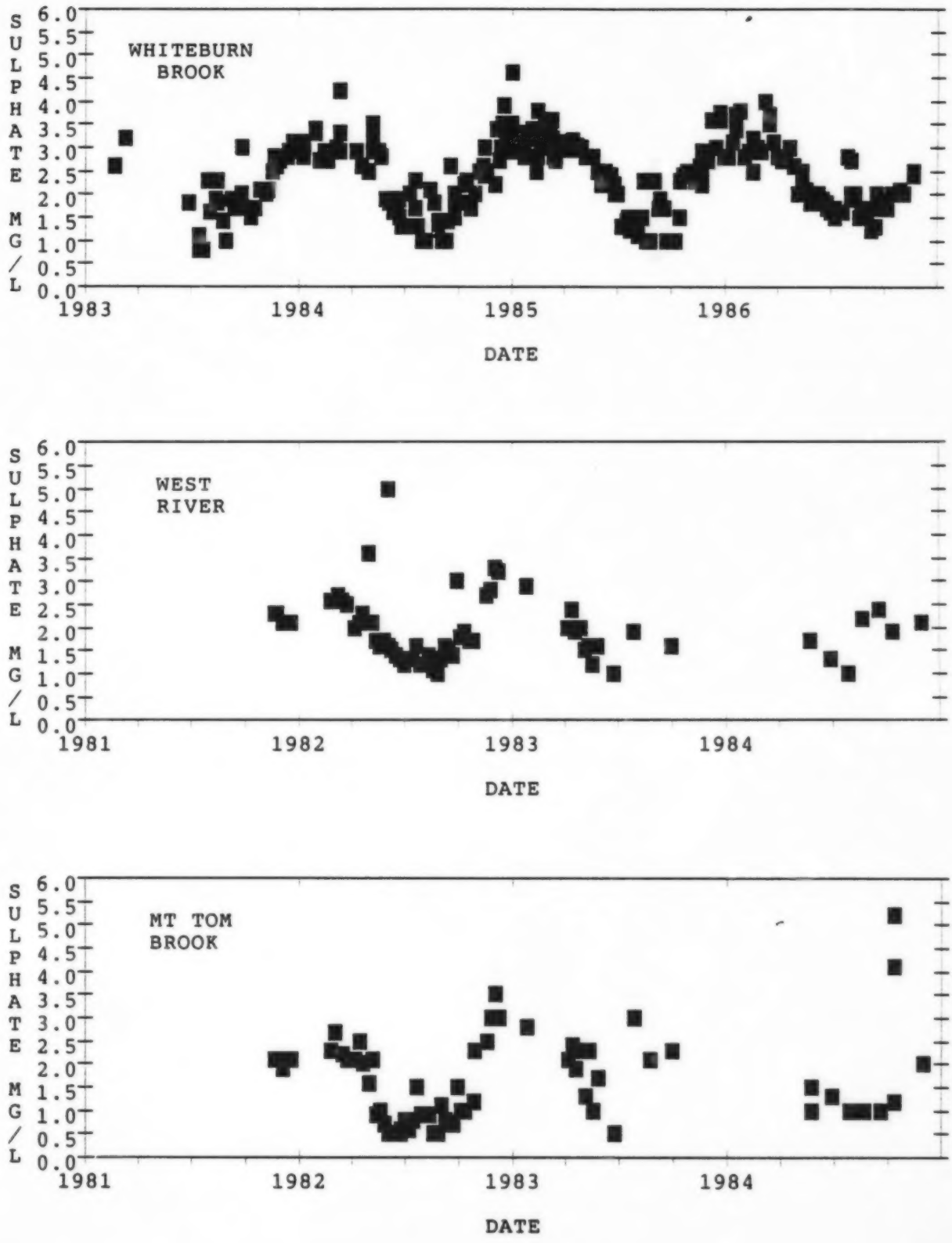


FIGURE 46: SULPHATE CONCENTRATIONS IN TWO HIGH ORDER RIVERS

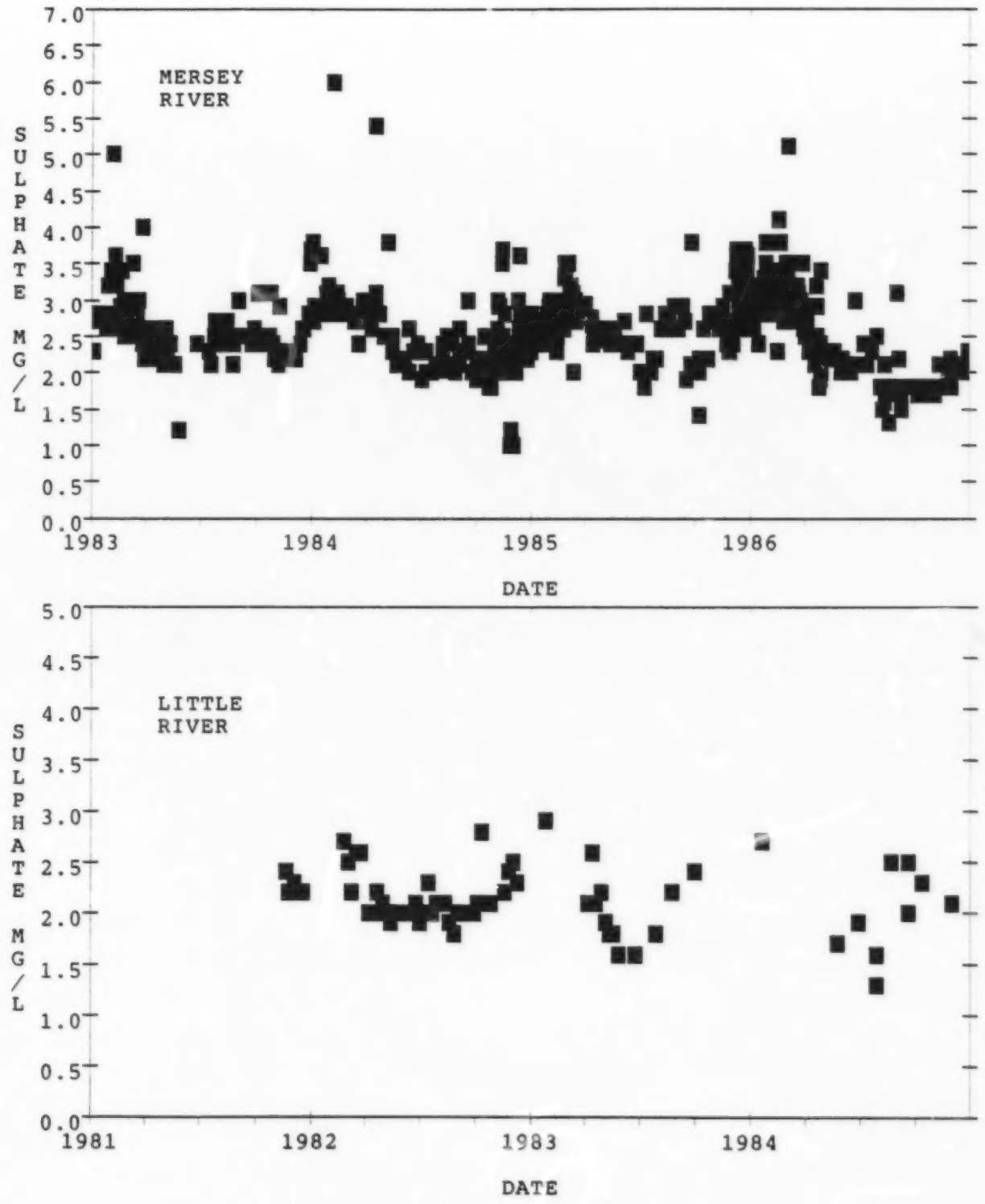


FIGURE 47: SULPHATE CONCENTRATIONS IN TWO HEADWATER LAKES

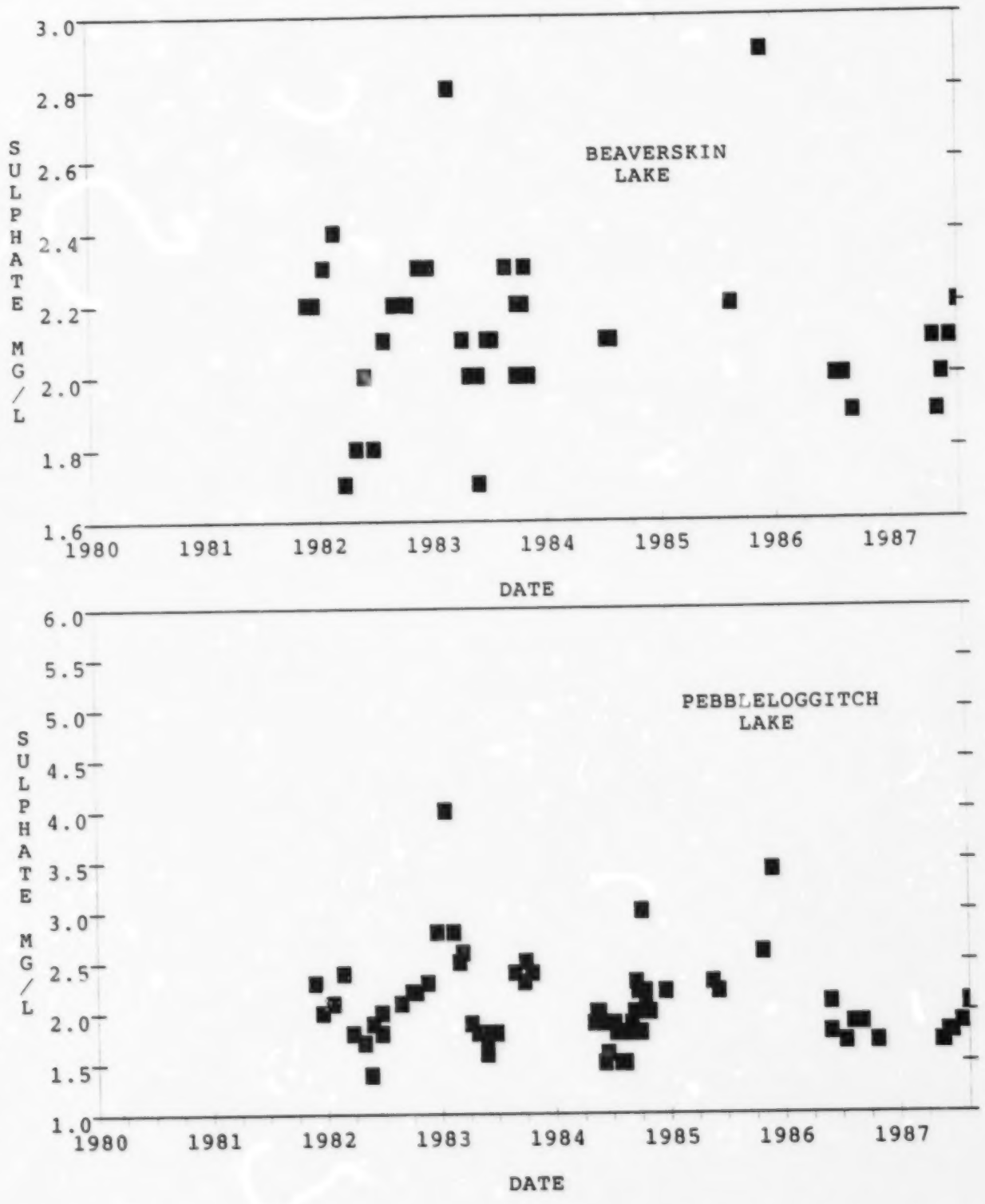


FIGURE 48 : SULPHATE CONCENTRATIONS IN WATER FROM PEBBLELOGGITCH WELL

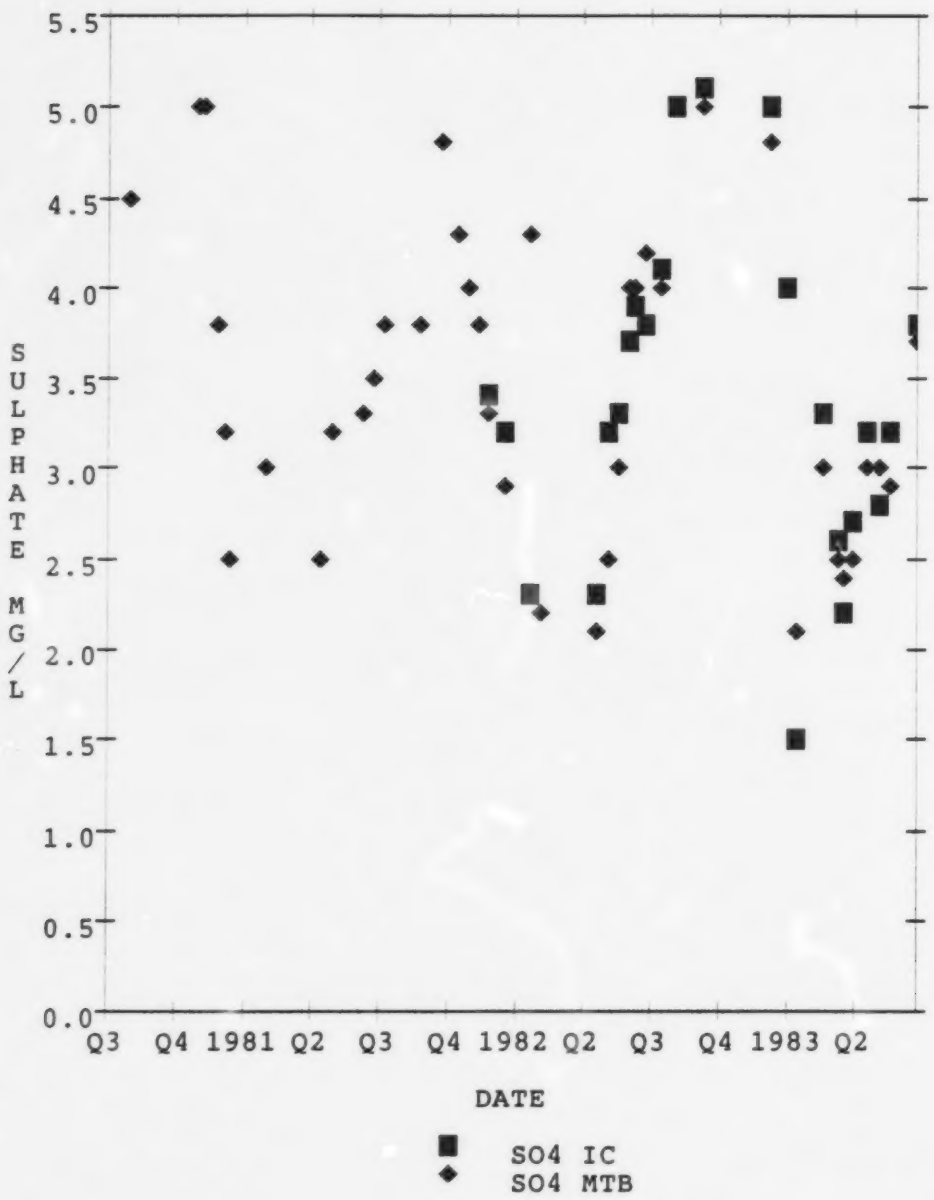


FIGURE 49: WET DEPOSITION AND MONTHLY EXPORT OF SULPHATE FROM MOOSE PIT BROOK

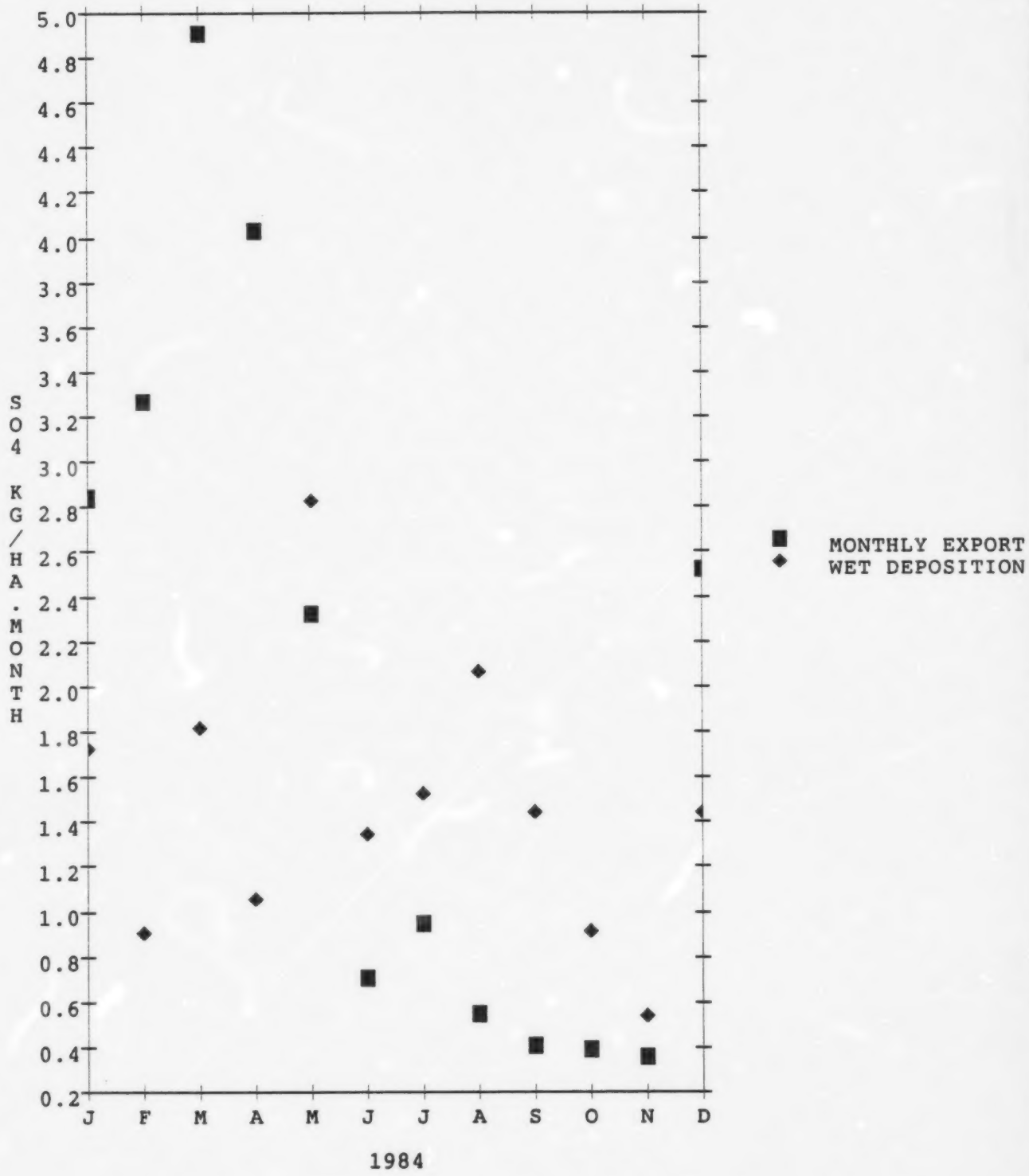


FIGURE 50: WET DEPOSITION AND MONTHLY EXPORT OF SULPHATE FROM THE MERSEY RIVER

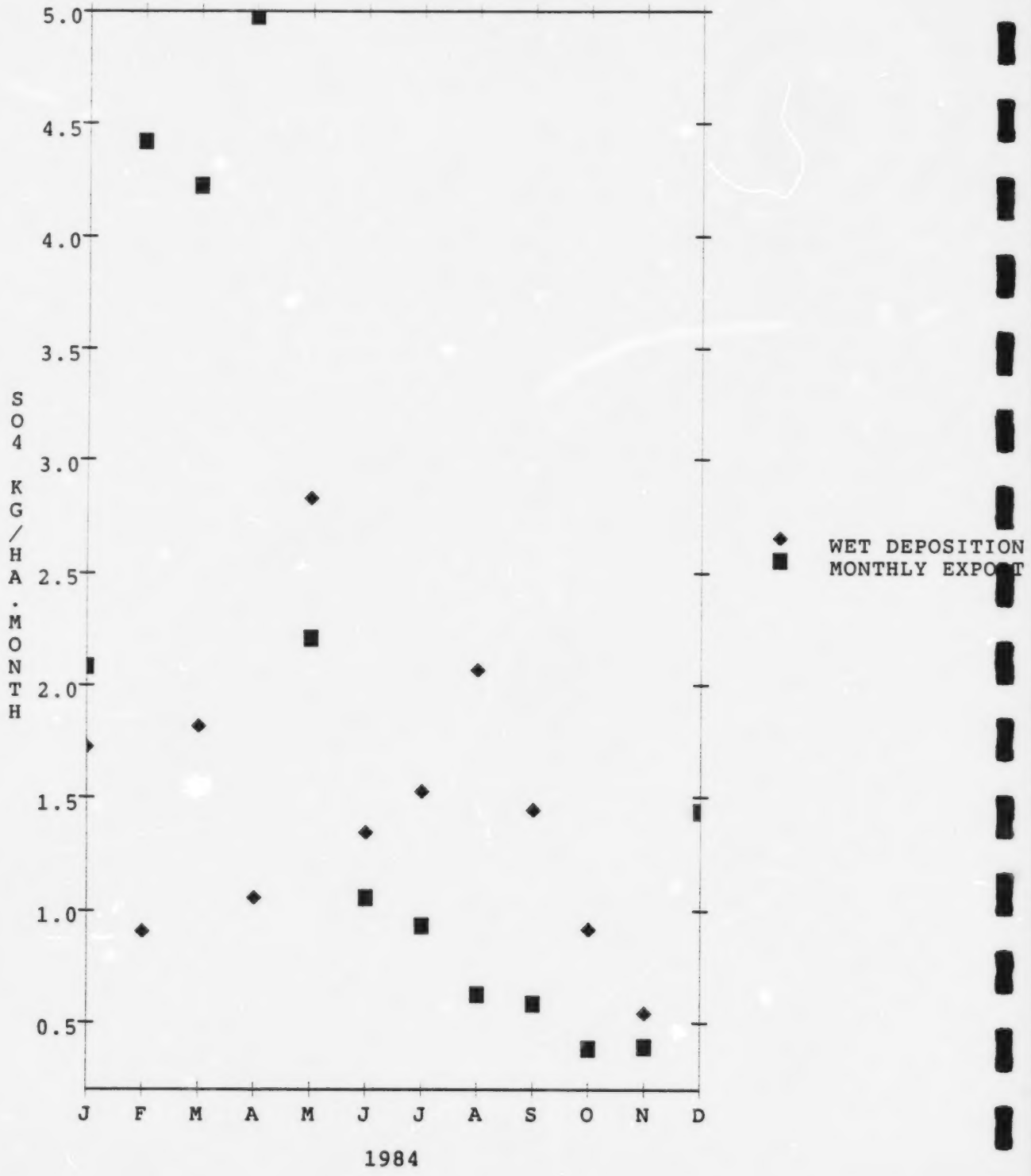


FIGURE 51: THE RATIO OF RUNOFF TO PRECIPITATION FOR THE MERSEY RIVER AND MOOSE PIT BROOK

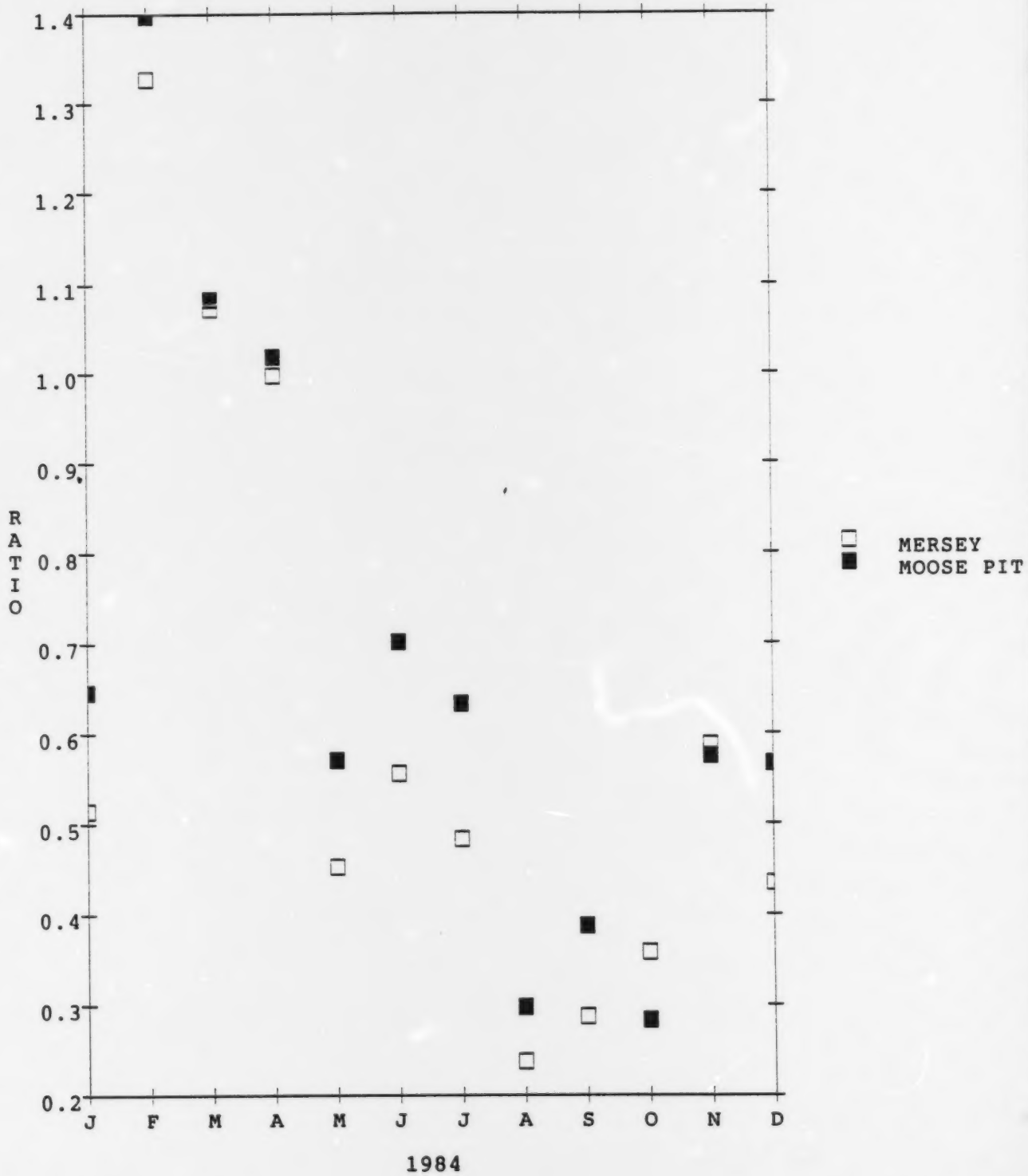
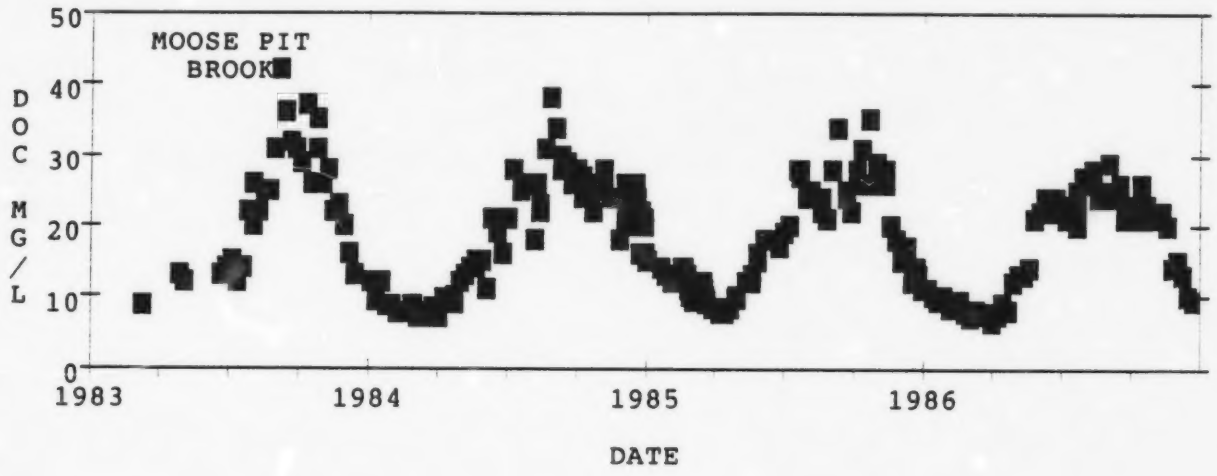
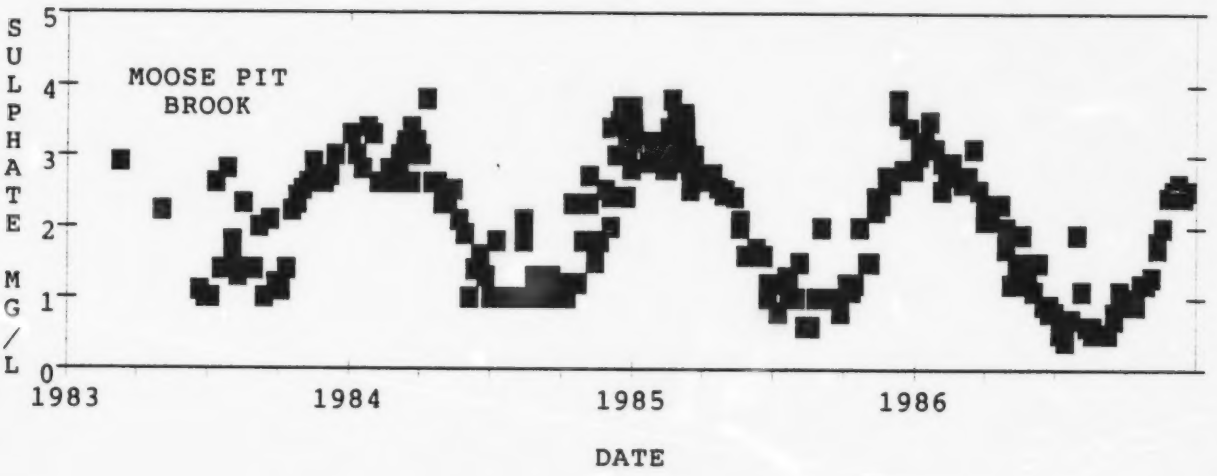


FIGURE 52: SEASONAL VARIABILITY OF DOC, SULPHATE AND pH FOR MOOSE PIT BROOK





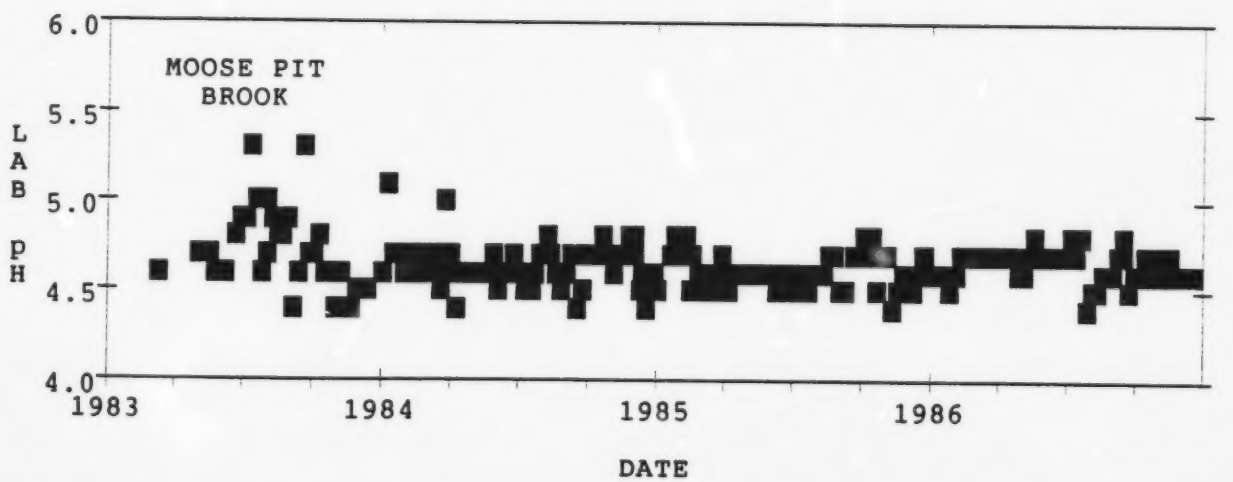


FIGURE 53: SEASONAL VARIABILITY OF DOC, SULPHATE AND pH FOR RODGERS BROOK

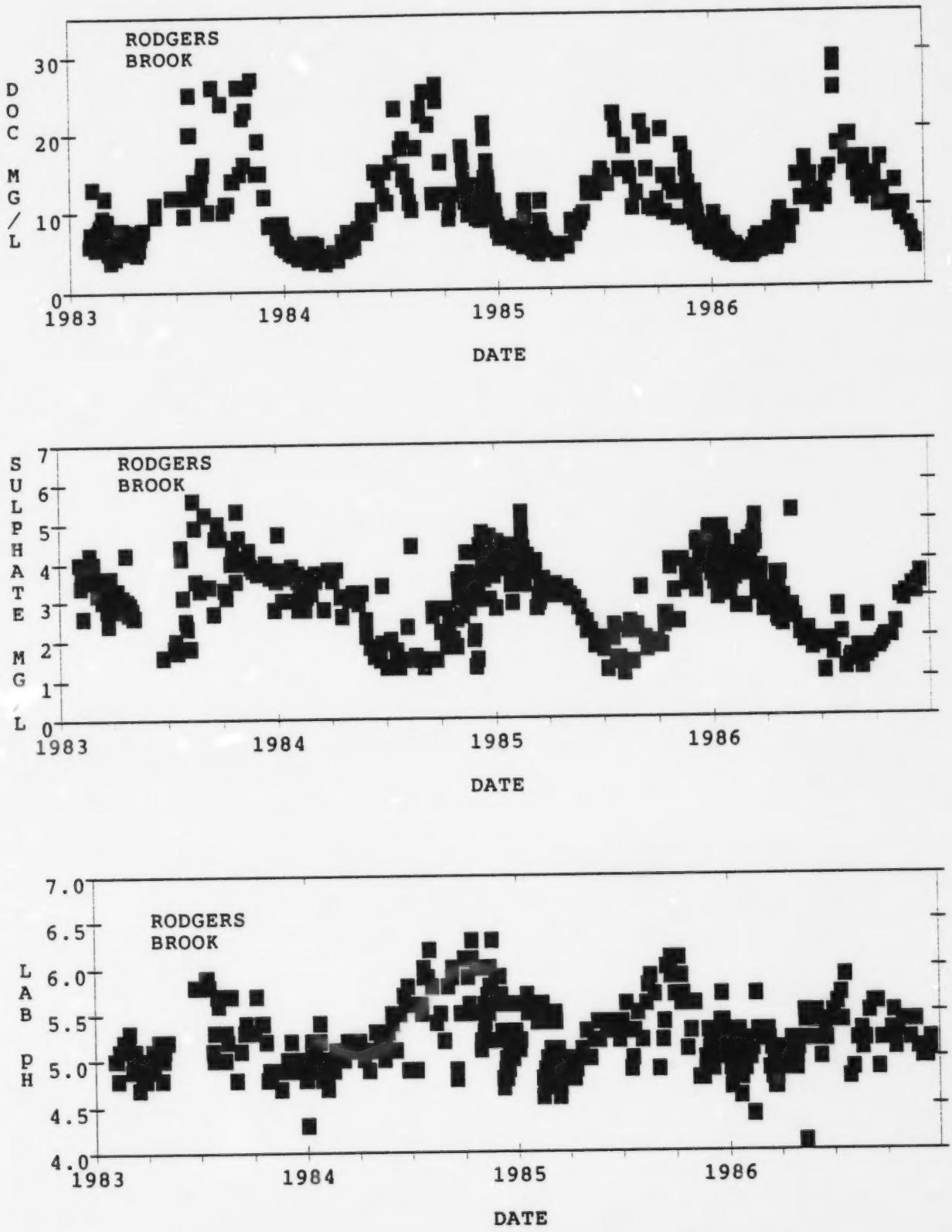


FIGURE 54: SEASONAL VARIABILITY OF DOC, SULPHATE AND pH FOR ATKINS BROOK

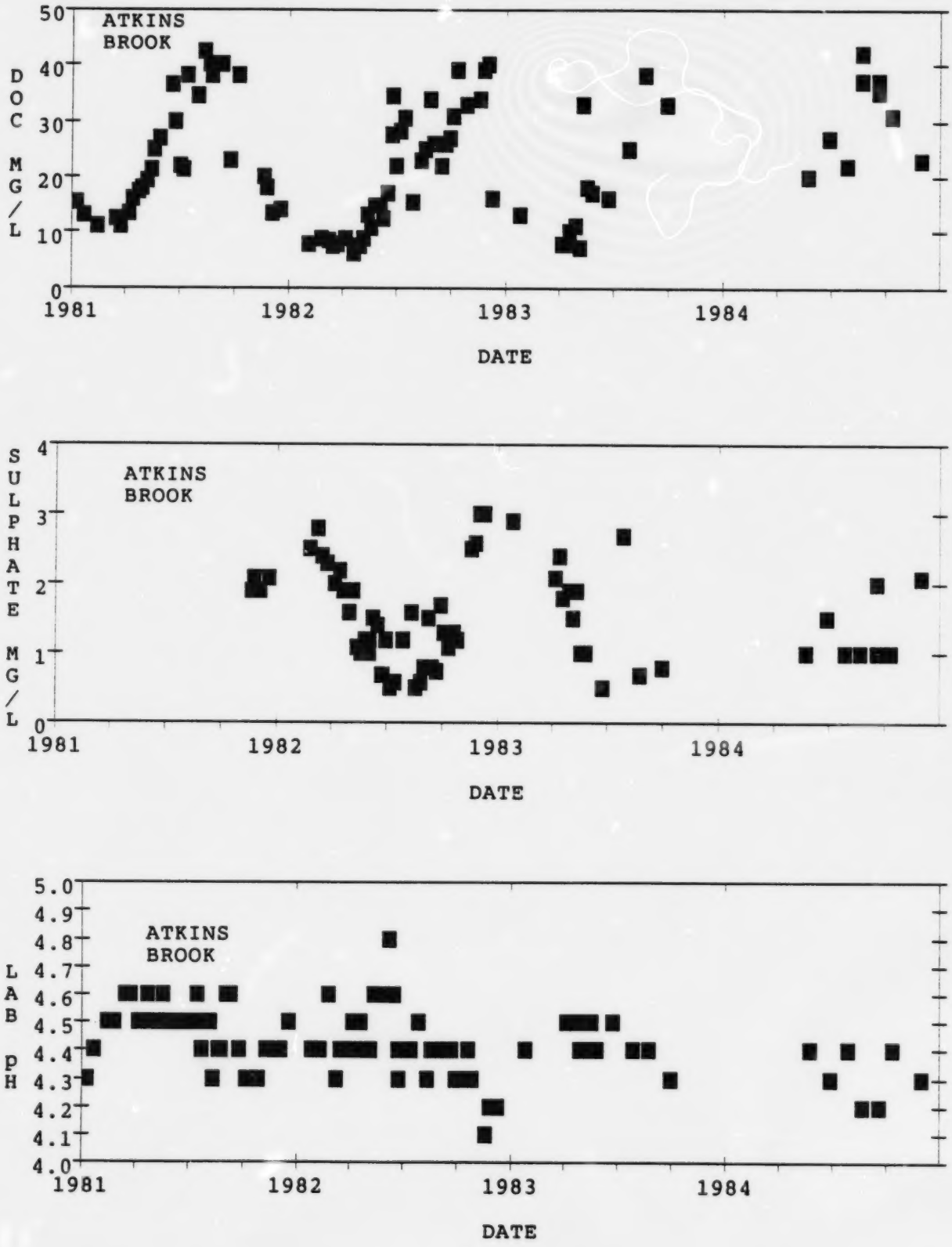


FIGURE 55: SEASONAL VARIABILITY OF DOC, SULPHATE AND pH FOR MOUNT TOM BROOK

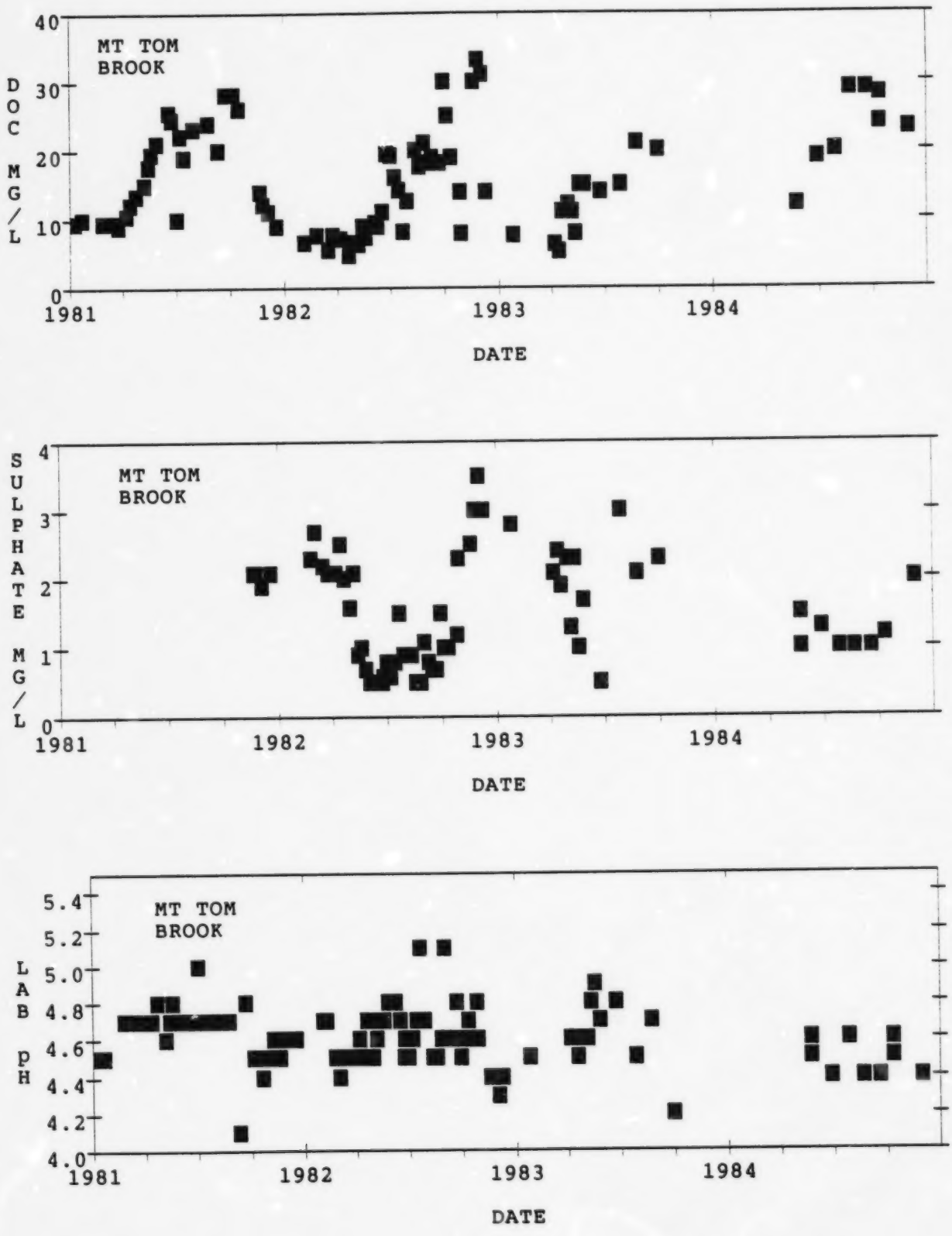


FIGURE 56: SEASONAL VARIABILITY OF DOC, SULPHATE AND pH FOR WHITEBURN BROOK

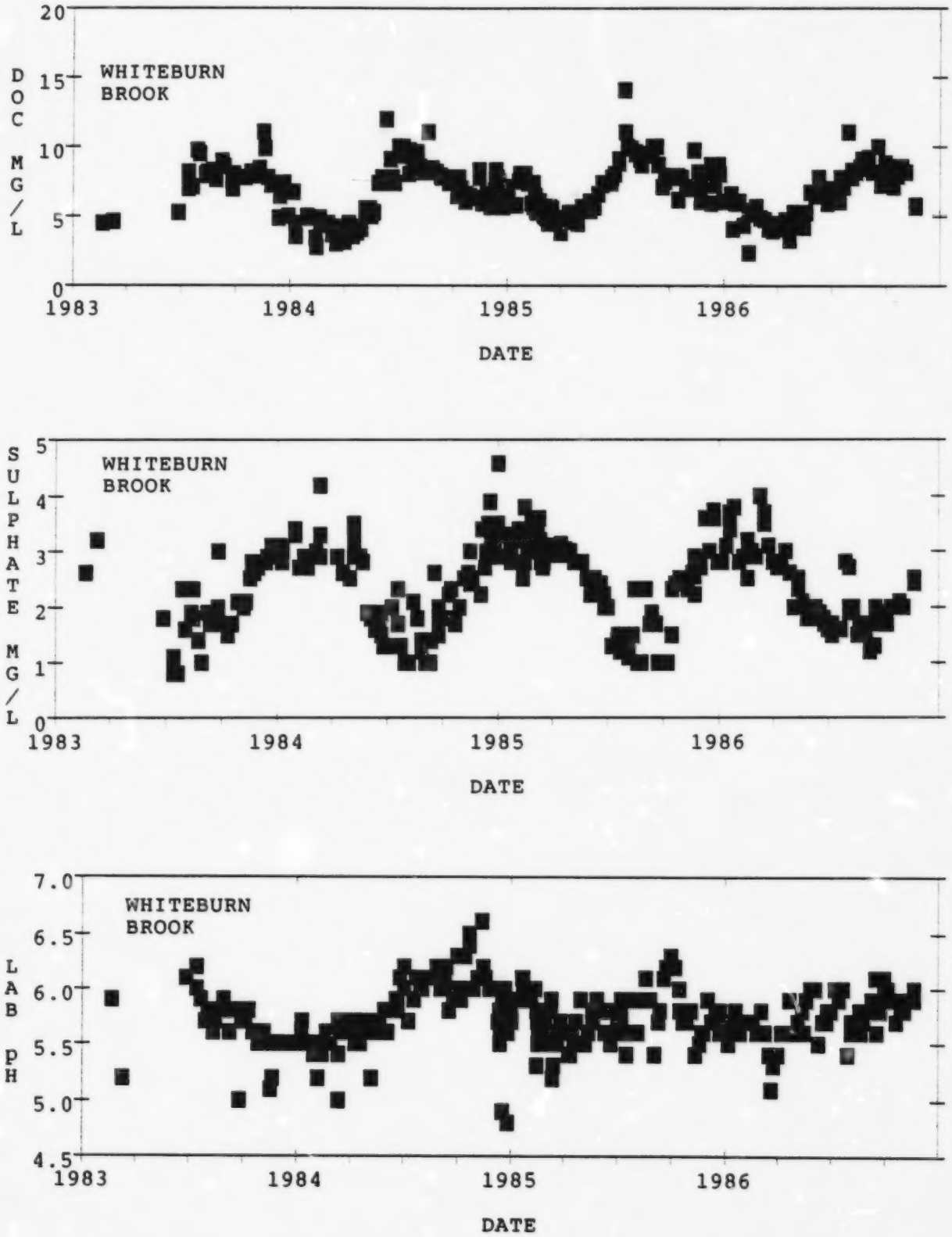


FIGURE 57: SEASONAL VARIABILITY OF DOC, SULPHATE AND pH FOR WEST RIVER

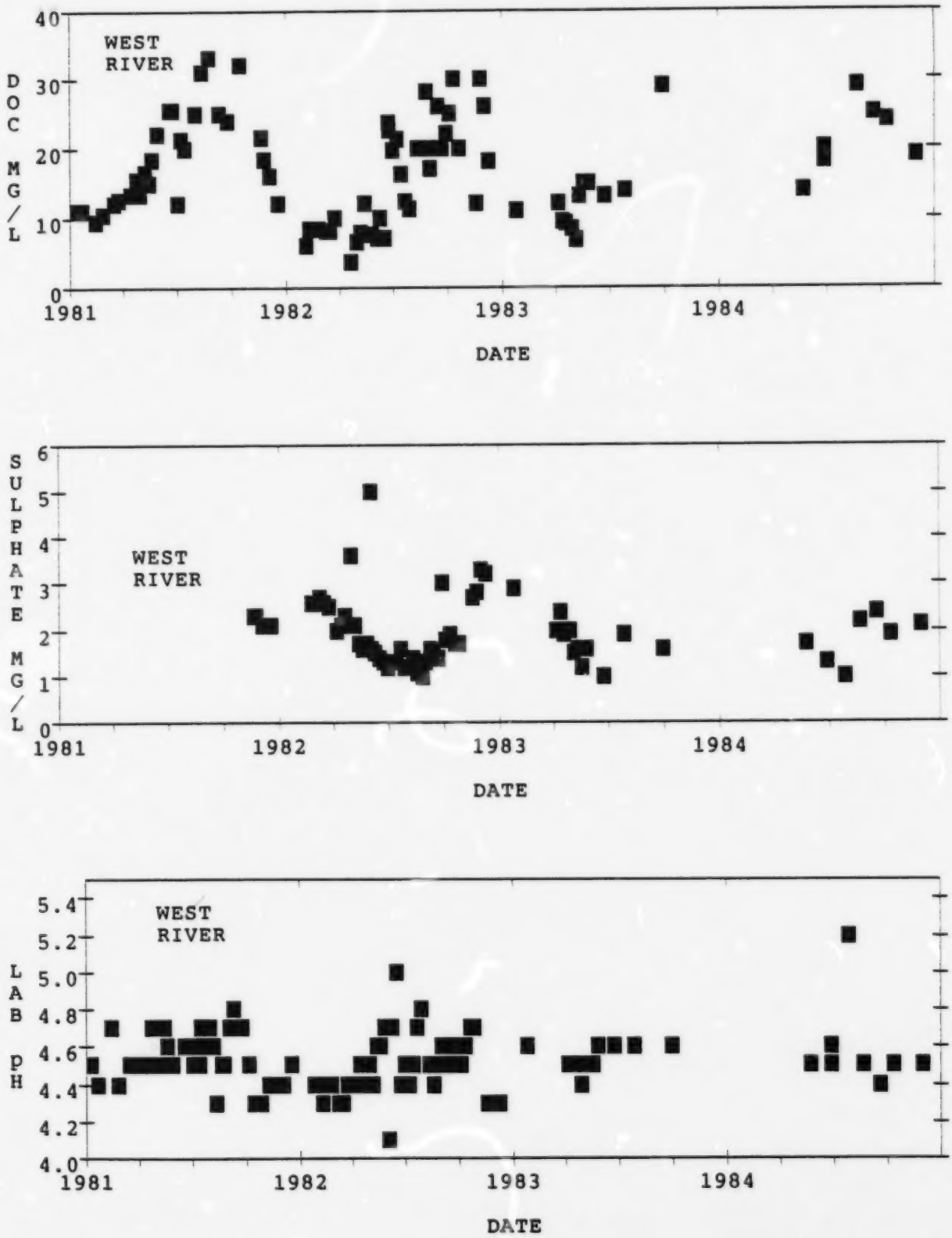


FIGURE 58: ORGANIC BUFFERING POTENTIAL OF MOOSE PIT BROOK

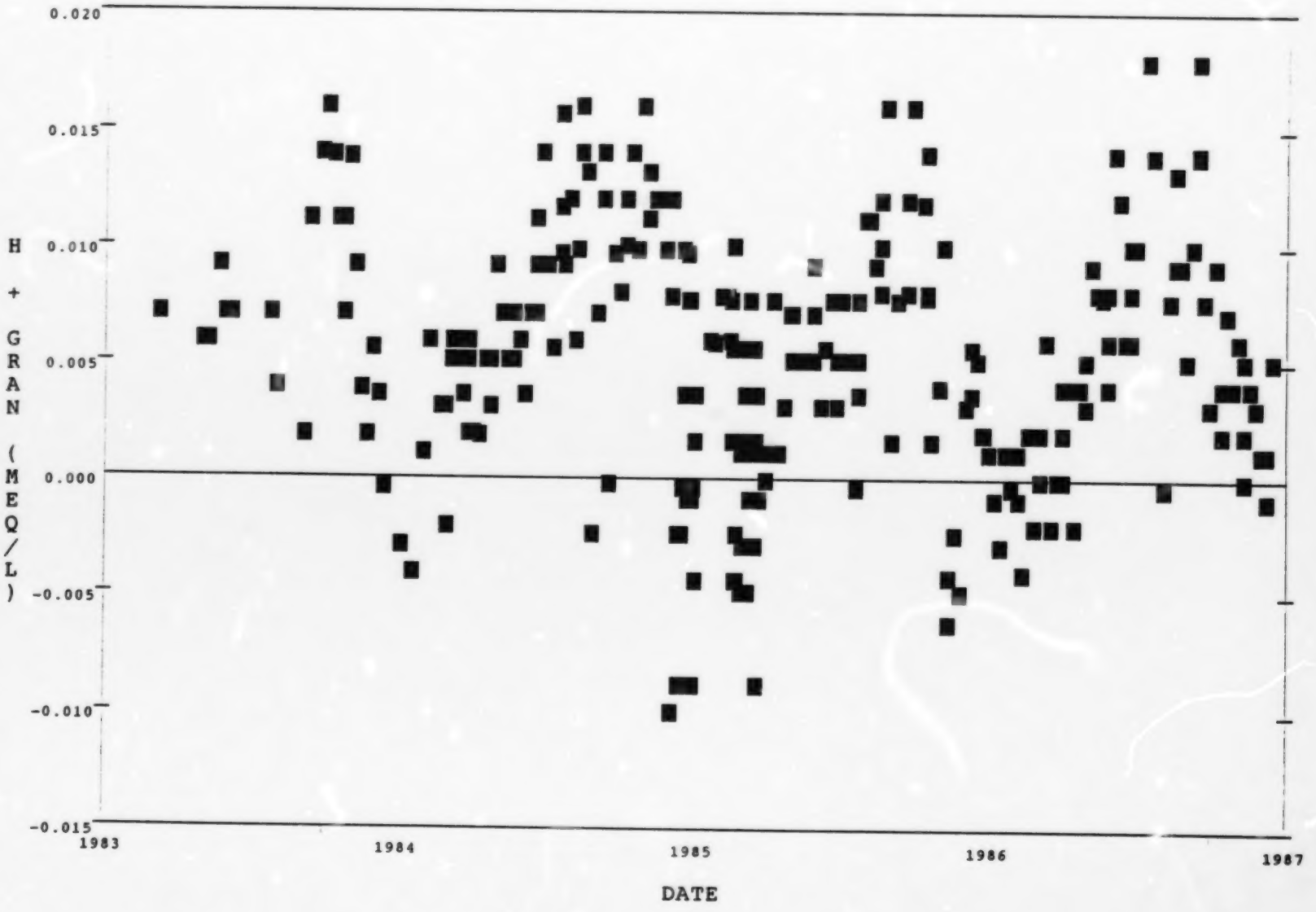


FIGURE 59: RELATIVE CONTRIBUTION OF MINERAL
AND ORGANIC ACIDS TO THE ACIDIFICATION OF MOOSE PIT BROOK

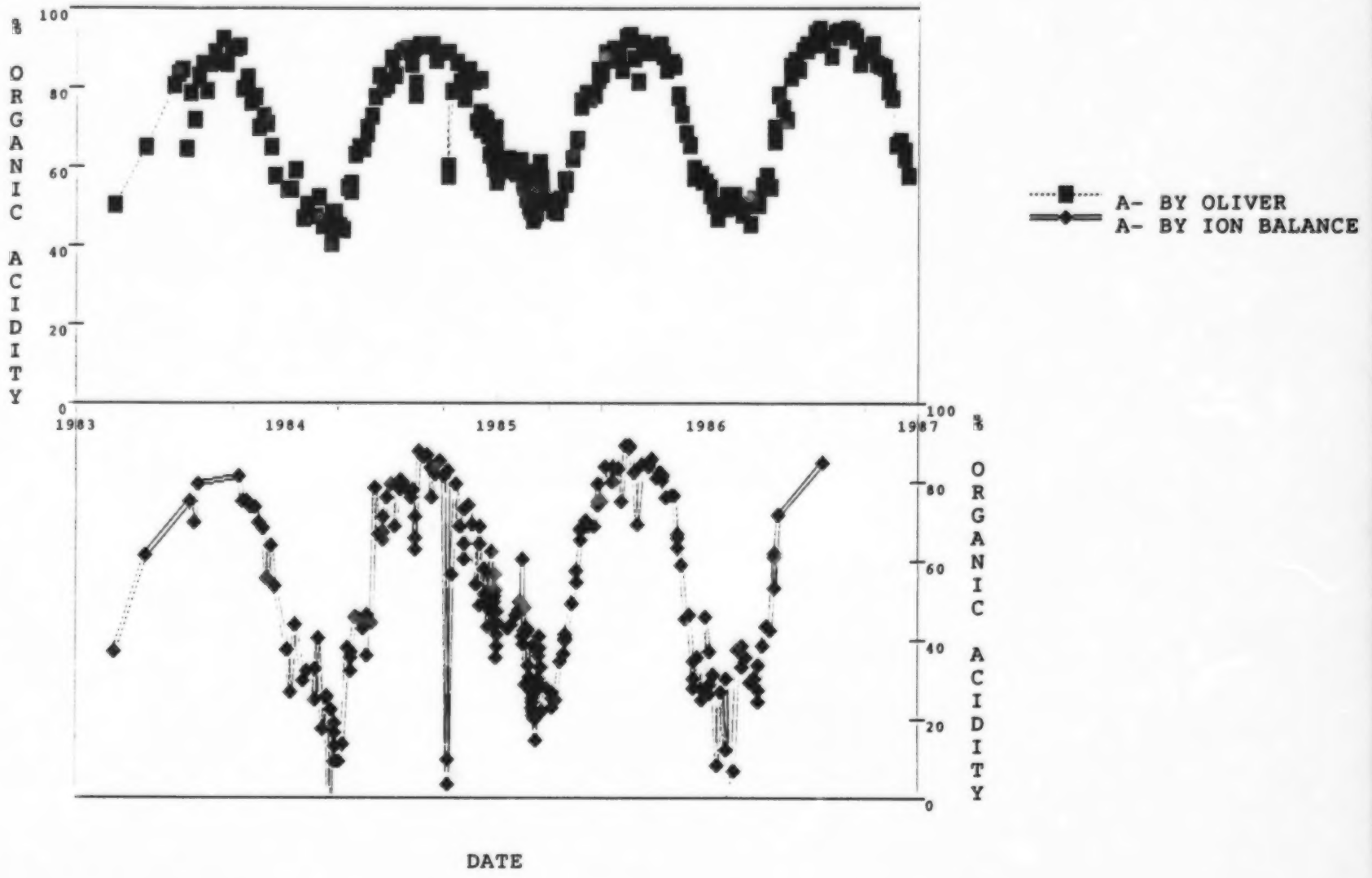


FIGURE 60: SEASONAL VARIABILITY OF DOC, SULPHATE AND pH FOR THE MERSEY RIVER

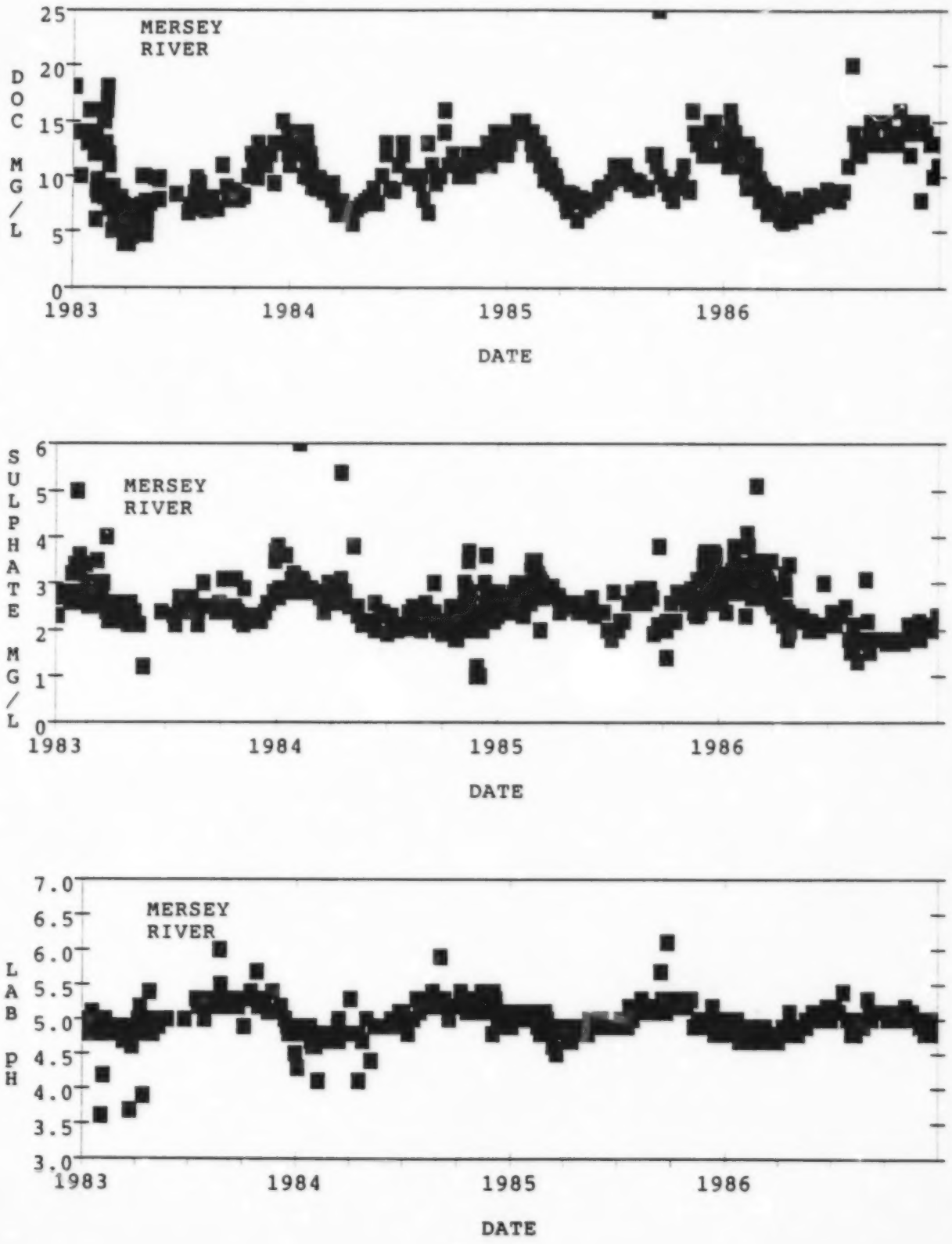


FIGURE 61: SEASONAL VARIABILITY OF DOC, SULPHATE AND pH FOR LITTLE RIVER

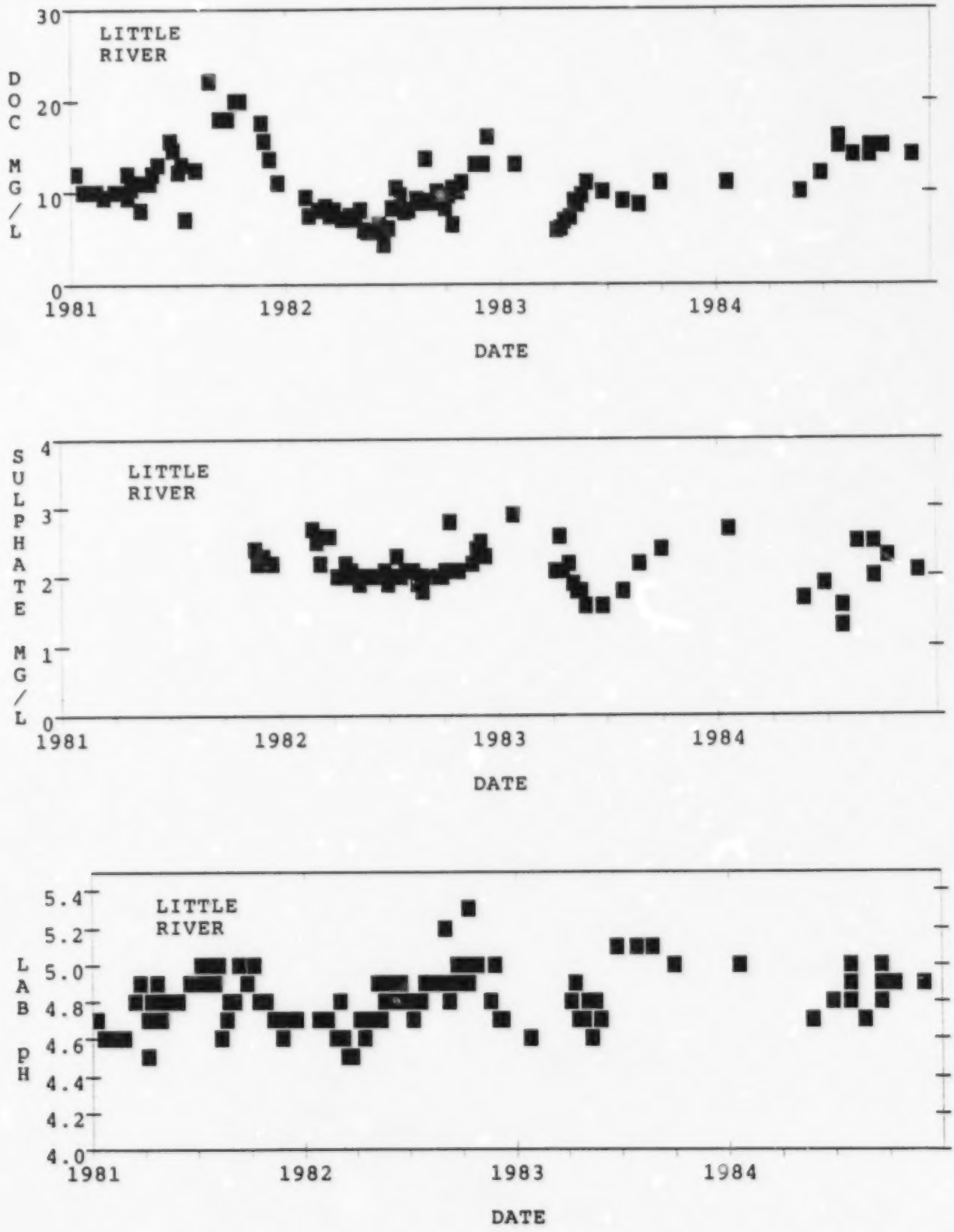


FIGURE 62: RELATIVE CONTRIBUTION OF MINERAL AND ORGANIC ACIDS TO THE ACIDIFICATION OF THE MERSEY RIVER

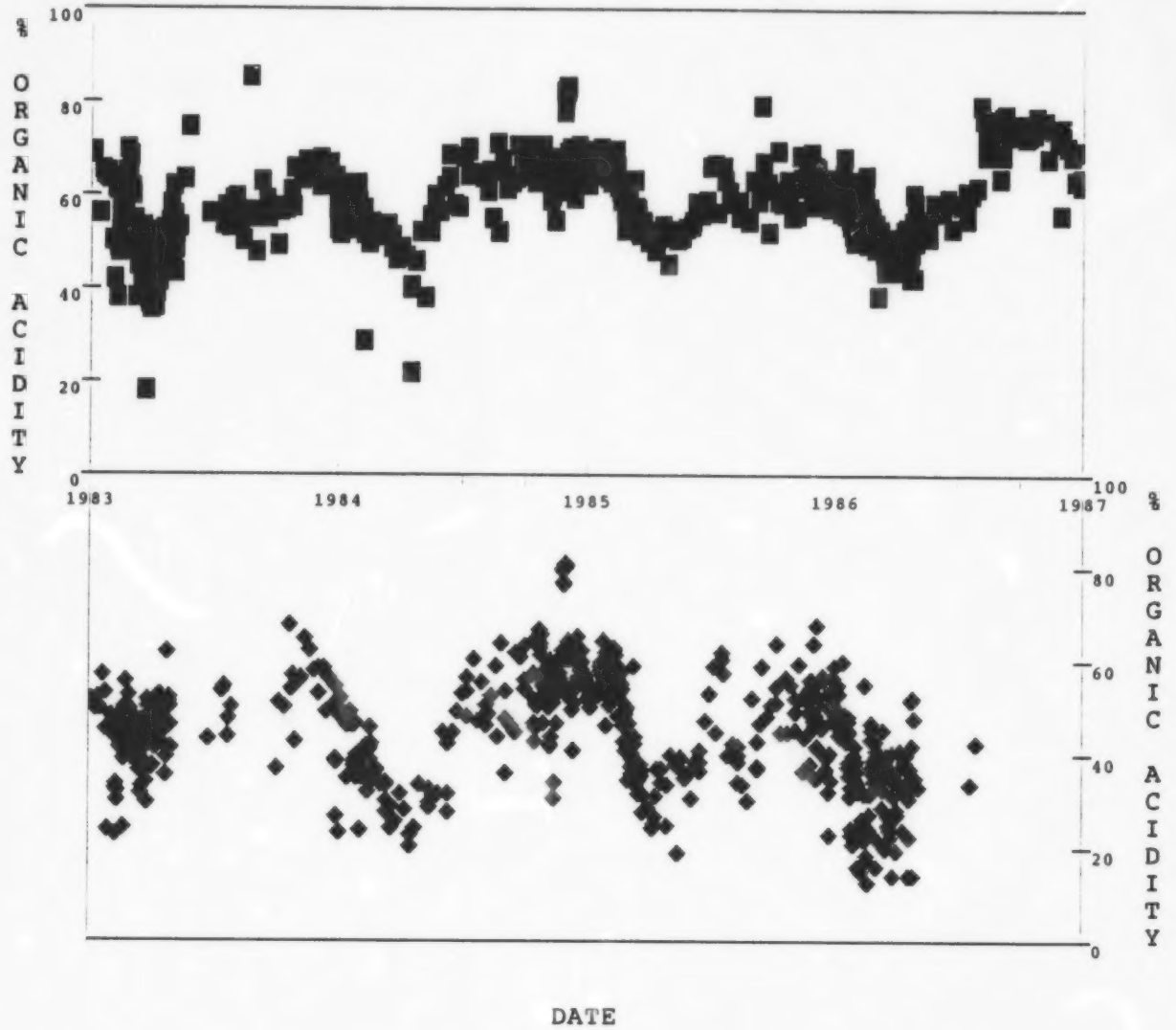


FIGURE 63: RESULTS OF PRINCIPLE COMPONENT ANALYSIS FOR THE MERSEY RIVER AND MOOSE PIT BROOK

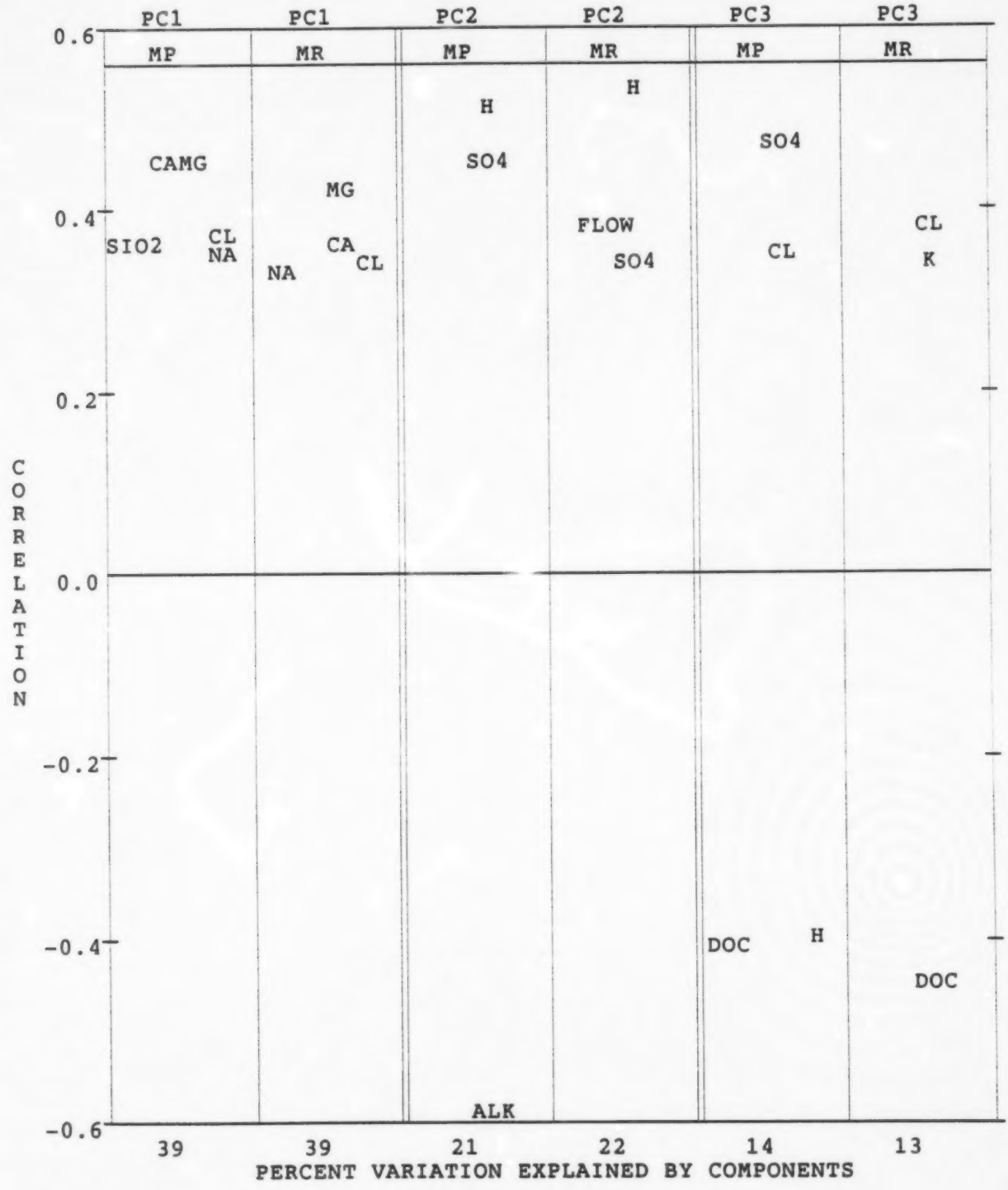


FIGURE 64: PRINCIPLE COMPONENKT SCORES (PC #1 VERSUS PC #2) FOR THE MERSEY RIVER PLOTTED BY MONTH

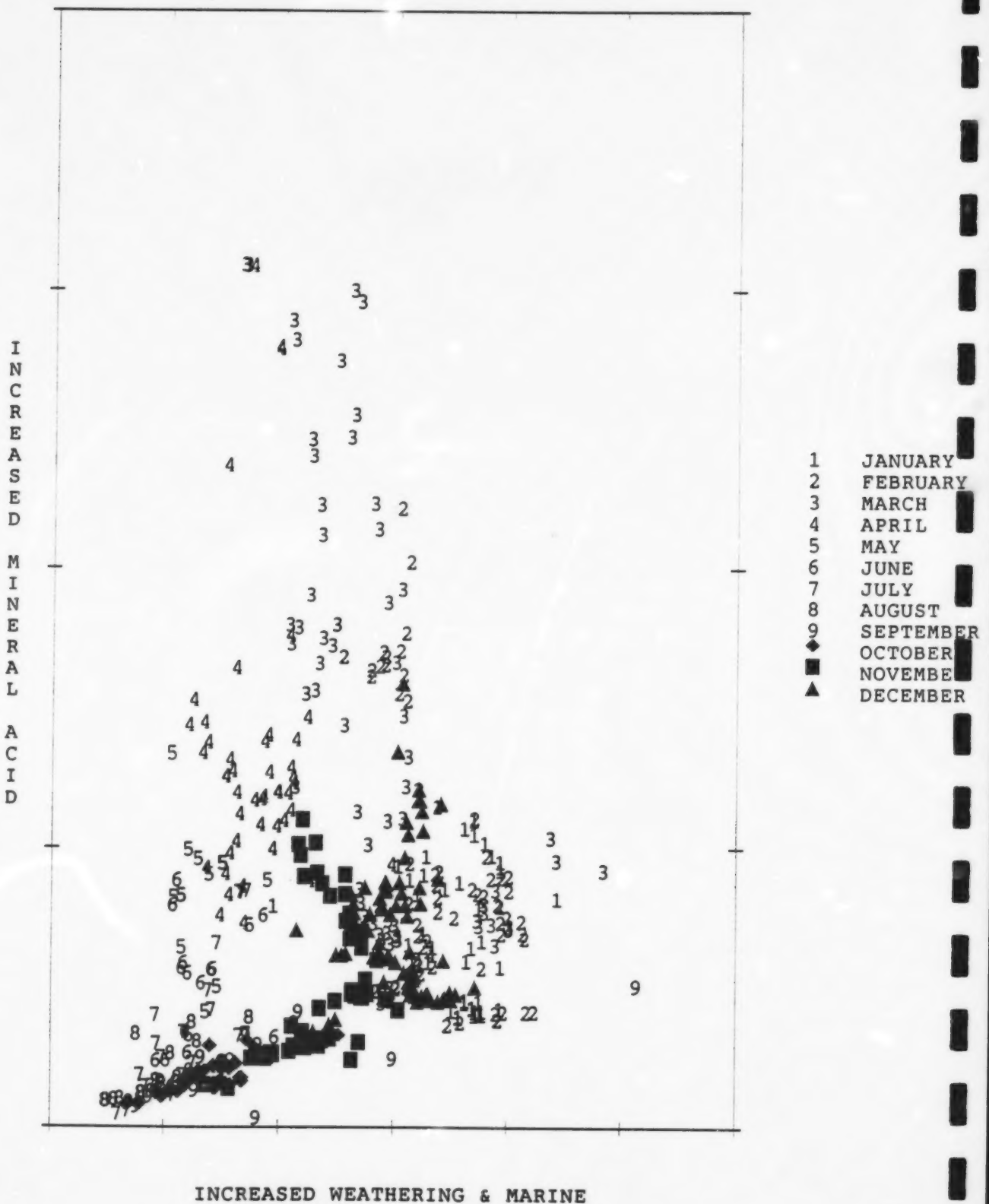


FIGURE 65: PRINCIPLE COMPONENT SCORES (PC #1 VERSUS PC #2) FOR MOOSE PIT BROOK PLOTTED BY MONTH

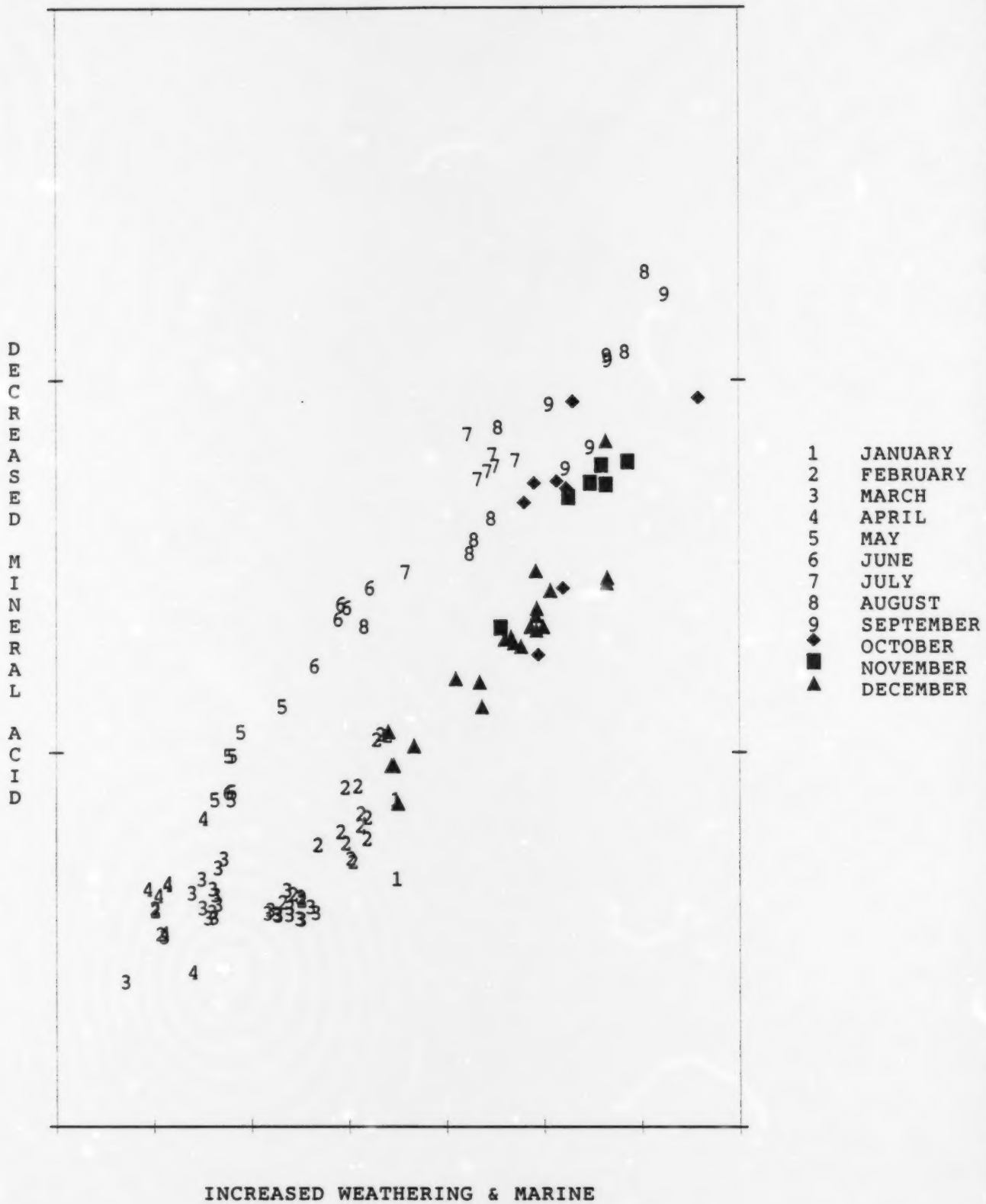


FIGURE 66: PRINCIPLE COMPONENT SCORES (PC #2 VERSUS PC #3) FOR MOOSE PIT BROOK PLOTTED BY MONTH